

PHYSICAL
SCI. LIB.

TN
24
C3
A33
NO. 138

DISTRIBUTION OF HEAVY ELEMENTS HAZAR-
DIOUS TO HEALTH, SALINAS VALLEY REGION,
CA. By: Hasmukhrai H. Majmudar.

U.C.D. LIBRARY

DISTRIBUTION OF HEAVY ELEMENTS HAZARDOUS TO HEALTH, SALINAS VALLEY REGION, CALIFORNIA

1980

CALIFORNIA DIVISION OF MINES AND GEOLOGY

SPECIAL REPORT 138



UNIVERSITY OF CALIFORNIA
DAVIS
APR 14 1981
LIBRARY

UNIVERSITY OF CALIFORNIA
DAVIS
APR 13 1981
CALIF. DEPOS.
GOVT. DOCS. - LIBRARY

U.C. LIBRARY



STATE OF CALIFORNIA
EDMUND G. BROWN JR.
GOVERNOR

THE RESOURCES AGENCY
HUEY D. JOHNSON
SECRETARY FOR RESOURCES

DEPARTMENT OF CONSERVATION
PRISCILLA C. GREW
DIRECTOR

DIVISION OF MINES AND GEOLOGY
JAMES F. DAVIS
STATE GEOLOGIST

Special Report 138

DISTRIBUTION OF
HEAVY ELEMENTS HAZARDOUS TO HEALTH,
SALINAS VALLEY REGION, CALIFORNIA

By
Hasmukhrai H. Majmundar
Geochemist

1980

CALIFORNIA DIVISION OF MINES AND GEOLOGY
1416 Ninth Street, Room 1341
Sacramento, CA 95814

CONTENTS

	Page
ABSTRACT	v
INTRODUCTION	1
GEOLOGY	2
DEVELOPMENT OF SAMPLING AND ANALYTICAL PROCEDURES	4
Sampling techniques	4
Sample preparation.....	4
Digestion	4
Stream sediment samples	4
Bedrock samples	4
Analytical techniques.....	4
Mercury	4
Arsenic	7
Cadmium, copper, lead, and zinc	7
Phosphorus	7
RESULTS OF ANALYSES	8
Mercury	8
Arsenic.....	8
Cadmium	8
Lead.....	8
Copper and zinc	9
Phosphorus.....	9
CORRELATION.....	9
CONCLUSIONS	29
RECOMMENDATION	31
ACKNOWLEDGMENTS	31
REFERENCES	31
APPENDIX A. Locations of stream sediment samples	32
APPENDIX B. Locations of bedrock samples	33
APPENDIX C. Computer programs	35
APPENDIX D. Digestion procedures	37
APPENDIX E. Analytical techniques	39
APPENDIX F. Chemical analyses of stream sediments.....	47
APPENDIX G. Chemical analyses of bedrocks.....	48
APPENDIX H. Precision and accuracy of the analytical techniques	50
APPENDIX I. Statistical treatment of data.....	51

ILLUSTRATIONS

Figures

	Page
Figure 1. Index map of drainage basins in Salinas Valley	3
Figure 2. Index map of locations of stream sediment samples, Salinas Valley	5
Figure 3. Index map of locations of bedrock and same stream sediment samples from Salinas Valley	6
Figure 4. Technique for collecting composite stream sediment samples	7
Figure 5. Arsenic in stream sediments	10
Figure 6. Arsenic in bedrocks and same stream sediments	11
Figure 7. Cadmium in stream sediments	12
Figure 8. Cadmium in bedrocks and some stream sediments	13
Figure 9. Copper in stream sediments	14
Figure 10. Copper in bedrocks and same stream sediments	15
Figure 11. Lead in stream sediments	16
Figure 12. Lead in bedrocks and same stream sediments	17
Figure 13. Mercury in stream sediments	18
Figure 14. Mercury in bedrocks and same stream sediments	19
Figure 15. Phosphorus in bedrocks and same stream sediments ..	20
Figure 16. Zinc in stream sediments	21
Figure 17. Zinc in bedrocks and same stream sediments	22
Figure 18. Correlation between arsenic and cadmium in stream sediments	23
Figure 19. Correlation between arsenic and copper in stream sediments	23
Figure 20. Correlation between arsenic and zinc in stream sediments	24
Figure 21. Correlation between cadmium and copper in stream sediments	24
Figure 22. Correlation between cadmium and zinc in stream sediments	25
Figure 23. Correlation between copper and zinc in stream sediments	25
Figure 24. Correlation between cadmium and copper in bedrocks ..	26
Figure 25. Correlation between cadmium and phosphorus in bedrocks	26
Figure 26. Correlation between cadmium and zinc in bedrocks ..	27
Figure 27. Correlation between phosphorus and copper in bedrocks	27
Figure 28. Correlation between copper and zinc in bedrocks	28
Figure 29. Correlation between phosphorus and zinc in bedrocks ..	28
Figure 30. Digestion apparatus for volatile elements	37
Figure 31. Non-flame mercury device	39
Figure 32. Working curve for mercury	41
Figure 33. Arsenic generation apparatus	41
Figure 34. Working curve for arsenic	43
Figure 35. Working curve for P ₂ O ₅ (high phosphate)	45
Figure 36. Working curve for P ₂ O ₅ (low phosphate)	45
Figure 37. Cumulative frequency distribution for arsenic in stream sediments	52
Figure 38. Cumulative frequency distribution for arsenic in bedrocks	52


Figure 39. Cumulative frequency distribution for cadmium in stream sediments	52
Figure 40. Cumulative frequency distribution for cadmium in bedrocks	52
Figure 41. Cumulative frequency distribution for copper in stream sediments	52
Figure 42. Cumulative frequency distribution for copper in bedrocks	52
Figure 43. Cumulative frequency distribution for lead in stream sediments	52
Figure 44. Cumulative frequency distribution for lead in bedrocks	52
Figure 45. Cumulative frequency distribution for mercury in stream sediments	52
Figure 46. Cumulative frequency distribution for mercury in bedrocks	52
Figure 47. Cumulative frequency distribution for phosphorus in stream sediments	52
Figure 48. Cumulative frequency distribution for zinc in stream sediments	52
Figure 49. Cumulative frequency distribution for zinc in bedrocks	52
Figure 50. Histogram for arsenic in stream sediments	52
Figure 51. Histogram for arsenic in bedrocks	52
Figure 52. Histogram for cadmium in stream sediments	52
Figure 53. Histogram for cadmium in bedrocks	52
Figure 54. Histogram for copper in stream sediments	52
Figure 55. Histogram for copper in bedrocks	52
Figure 56. Histogram for lead in stream sediments	52
Figure 57. Histogram for lead in bedrocks	52
Figure 58. Histogram for mercury in stream sediments	52
Figure 59. Histogram for mercury in bedrocks	52
Figure 60. Histogram for phosphorus in bedrocks	52
Figure 61. Histogram for zinc in stream sediments	52
Figure 62. Histogram for zinc in bedrocks	52

Tables

Table 1. Effects of anomalous levels of cadmium	52
Table 2. Predicted concentration of cadmium	52
Table 3. Correlation matrix (stream sediments)	52
Table 4. Correlation matrix (bedrocks)	52
Table 5. Correlation of geology and stream sediment chemistry	52
Table 6. Phosphorus and cadmium determinations in some other parts of the United States	52
Table 7. Correlation of geology and bedrock chemistry	52
Table 8. Comparison of various digestion techniques	52
Table 9. Precision tests for ten replications of samples 167/73, and N.B.S.120a	52
Table 10. Accuracy of arsenic, copper, lead, mercury, and phosphorus analyses	52
Table 11. Various parameters calculated on the basis of cumulative frequency curves	52

ABSTRACT

Samples of stream sediment and bedrock from the Salinas Valley region were analyzed to determine the distribution and the amounts of potentially health-hazardous heavy elements (arsenic, cadmium, copper, lead, mercury, and zinc). Cadmium was found to be anomalously high in the stream sediments and soils in the King City-San Ardo area in the extreme southeast corner of the project area. The California Department of Agriculture obtained similar high-cadmium values in samples of agricultural soils from the same area. The stream sediments appear to be derived from Middle Miocene marine strata exposed in the drainage basin. The source of the anomalous cadmium in these stream sediments in the King City-San Ardo area was traced to relatively thin beds of phosphatic rocks. Cadmium might exist in the phosphatic rocks elsewhere in the United States, and, because of the potential health hazard from cadmium, these other phosphatic rocks should be evaluated for possible cadmium contamination.



Digitized by the Internet Archive
in 2012 with funding from
University of California, Davis Libraries

<http://archive.org/details/distributionofhe138majm>

DISTRIBUTION OF HEAVY ELEMENTS HAZARDOUS TO HEALTH, SALINAS VALLEY REGION, CALIFORNIA

By Hasmukhrai H. Majmundar¹

INTRODUCTION

In July 1971, Governor Ronald Reagan mandated an interagency public health project to determine the sources and distribution of certain health-affecting elements in the Salinas Valley. Participating in the study were a number of organizations representing State, local, and federal agencies and also the private sector. The project was coordinated by the Project Committee of the Monterey Basin Pilot Monitoring Project, composed of representatives of each of the participating State and local agencies. The project objective was to design an efficient and effective monitoring program for tracing the source, movement and fate of environmentally harmful substances, and to determine the extent to which such a program could be planned and implemented by a multitude of agencies with separate interests and responsibilities with regard to environmental quality.

The report presents the results of the California Division of Mines and Geology participation in the project. The Division's part in the project included (1) the development of accurate techniques for sampling the stream sediments of the project area; (2) the development of analytical procedures for detecting very small concentrations of arsenic, cadmium, and mercury; and (3) the preparation of maps showing the distribution of arsenic, cadmium, copper, lead, mercury, and zinc in the sediments of the Salinas Valley. These elements were selected for study because of their health-hazard characteristics.

Certain compounds of arsenic are poisonous when eaten in more than trace amounts, but little is known about their other characteristics, including their carcinogenic potential. Nevertheless, arsenic is generally well known to be an undesirable element from a health standpoint. Throughout the world arsenic is most abundant in areas in which sulfide deposit occurs.

Cadmium is a known cause of high blood pressure and has been identified as an extremely carcinogenic element (as has nickel). In its primary occurrence in nature, cadmium generally is associated as a trace impurity with lead-zinc sulfide mineral assemblages, and it can be expected to abound in areas containing such minerals. The phosphatic sediments in the Middle Miocene unit of the project area are known to contain zinc; and, as expected, the presence of cadmium in these phosphatic sediments was later confirmed by Project data.

Cadmium may be introduced into the environment by such industrial discharges as mine wastewater, smelter or refining exhausts, or electroplating wastes. It is also introduced when fertilizers containing phosphate rock are added to agricultural soils; such phosphate fertilizers contain 9 to 36 ppm Cd, which is absorbed in some grains and vegetables to the extent of 1 to 4 milligrams per hundred grams (mg/100g) (Furst and Haro, 1969). Superphosphate, another form of commercial fertilizer, can also be a source of cadmium in certain vegetables (Schroeder and Balassa, 1963).

Although the uptake of cadmium in plants is species dependent and certain crops can accumulate it much more readily than others, in general cadmium is retained in plants at concentrations ten times greater than those in animals. Older animals, however, because of the longer duration of their exposure, can have higher levels of concentration than plants. Strangely enough, children retain higher concentrations than adults.

The Monterey Basin Pilot Monitoring Project discovered that, in certain sections of the project area, elevated levels of cadmium are present in aquatic life as well as in terrestrial soils, plants, and animals. Filter-feeding organisms and scavengers living in the sediments were found to have the highest cadmium values.

Human beings can be exposed to cadmium via food, water, and air. Of these, however, exposure through food is by far the most significant. In uncontaminated areas, most foodstuffs contain less than 0.05 μg Cd/g wet weight, and the average daily intake probably is about 50 μg . Liver and kidney probably have concentrations larger than 0.05 $\mu\text{g}/\text{g}$. When foodstuff is contaminated by cadmium in soil and water, the cadmium concentrations may increase considerably. In water, the normal concentration of cadmium is less than 1 ng/g. If the cadmium concentration in drinking water exceeds 5 ng/g, it contributes a significant amount in daily uptake of cadmium. The normal concentration of cadmium in air is about 0.001 $\mu\text{g}/\text{m}^3$. In areas where cadmium-emitting factories are situated, average cadmium concentrations of 0.1 to 0.5 $\mu\text{g}/\text{m}^3$ have been recorded, which may result in the inhalation of 2 to 10 μg cadmium per day. Smoking also contributes to daily intake. Smoking one pack of cigarettes contributes 2 to 4 $\mu\text{g}/\text{d}$ intake. (Friberg and others, 1971; Sandstead and others, 1974).

Table 1 gives the effects of anomalous levels of cadmium on animals and plants. Environmental cadmium poisoning has been

¹California Division of Mines and Geology, San Francisco, CA

Table 1. *Effects of anomalous levels of cadmium.**

Environmental Level	Effects on Plants		Effects on Animals Other than Man		Effects on Man	
	Established	Conjectured	Established	Conjectured	Established	Conjectured
Low	Absorbed through plant roots	-	-	-	-	-
High	-	Toxic	Acute: Testicular hemorrhage, male sterility. Chronic; hypertension. Little transfer to cow's milk from oral dose	Interferes with utilization of Zn, Fe, and Cu. (Se prevents Cd-induced pregnancy toxemia.)	-	Hypertension. Competes w Zn at metallothion binding site kidney. Regional differences in human kidney (Japan and United States have higher levels).

*After Hopps, H.C. (1974).

established as the cause of an estimated 100 human deaths in Japan by itai-itai disease. Table 2 gives the predicted concentrations of cadmium in soils, municipal drinking water, and vegetables. The median values probably represent ordinary, adequate levels of cadmium in water, soils, and foods (Sandstead and others, 1974).

Table 2. *Predicted concentration of cadmium.**

	Median	Range
Soils, ppm	0.06	0.01 - 0.7
Finished Municipal Water, ppb	~1.0	< 1.0 - 10
Forge Grasses, ppm	0.37	0.03 - 2.4
Forge Legumes, ppm	0.04	0.04 - 0.05
Vegetables and Fruits, ppm	0.10	0.01 - 0.96

*Credited to Helen L. Cannon
By Hopps, H.C., 1974.

Copper and zinc, when ingested in the presence of each other, can be toxic in varying degrees to fish and to humans.

The high toxicity of lead has long been known. The hazard from naturally occurring lead is small compared to that of man-created lead contamination, mostly from tetraethyl lead gasoline.

Mercury is highly toxic and has been identified as a carcinogen (Furst and Haro, 1969). It concentrates in body tissues with age and has been the source of area-wide health problems. Mercury tends to concentrate in the internal body organs of animals (liver, kidneys), and in plants. The U.S. Geological Survey investigated mercury in air, water, soil, and rock, and its effect on man (Fleischer, and others, 1970). Most of the earth's crust contains little mercury (80 ppb Hg), but large amounts of mer-

cury are generally present in areas in which any type of soil deposit occurs. Mercury enters the atmosphere through natural disintegration and decomposition of mercury-bearing minerals. Mercury is removed from the atmosphere by rain and by absorption in particulate matter. The particulate matter may be temporarily suspended in streams or lakes, but it will settle to the bottom eventually.

The Division's study provides background data on the natural distribution of these six elements in the project area and can be used as a base level against which other participants in the project can monitor air, water, particulate matter suspended in air and water, agricultural soils, vegetables, milk, hospital and industrial discharges in Monterey County.

The California Department of Water Resources includes cadmium among the elements tested in their analyses of stream water samples during the project. However, Boron could not be analyzed for lack of a sensitive analytical procedure to measure its presence in stream sediment samples.

As indicated by analyses of the stream sediments, a high portion of cadmium is present in sediments and soils near San Ardo. An effort was made to trace the source of this cadmium by collecting bedrock samples from this area. The bedrock samples also were analyzed for arsenic, cadmium, copper, lead, mercury, and zinc. The proportion of cadmium found to be high in some of the phosphatic beds. Therefore, the bedrock samples containing more than 10 ppm Cd also were analyzed for phosphorus in order to determine the correlation between the two. It was established that there is a very strong correlation between these two elements; when one element is higher, the other seems to be higher.

GEOLOGY

The geological framework of the project area is described by Hart (1966) and Durham (1964, 1966, and 1970) and shown on open-file maps by Dibblee (1967, 1968, 1969, 1971 and 1972) and the Geologic Map of California (Jennings and Strand, Jennings, 1958). The Salinas River drainage area extends

(miles southeast of this project area (Figure 1), but the main formations in the project area are pre-Cretaceous metamorphic rocks, Upper Cretaceous granitic intrusive rocks, and Tertiary Pliocene marine and nonmarine sedimentary rocks.

The pre-Cretaceous rocks are known as the Sur Series and consist of crystalline limestone and dolomite, quartzite, schist, gneiss, and various contact metamorphic rocks. They are the oldest rocks of the project area and are located on the segment of the west flank of the Salinas Valley that lies roughly between San Juan and Salinas.

Upper Cretaceous granitic rocks are predominant in the Gabilan Range on the northeast flank of the Salinas Valley, extending roughly from King City past Salinas.

The Tertiary and Plio-Pleistocene units occupy the southern two-thirds of the project area on both flanks of the Salinas Valley and the San Antonio and Nacimiento River drainage basins. The predominant Tertiary unit is the Miocene Monterey Formation, consisting mainly of siliceous and clayey shale and sandstone beds. In the Monterey Formation, phosphatic beds and petroliferous clay shale occur separately in various localities. The Monterey rocks and minor Plio-Pleistocene Paso Robles continental sandstone, conglomerate, and clay occur mainly in the southwest part of the project area — on the west flank of the Salinas Valley and in the basins of the San Antonio and Nacimiento Rivers. The principal Pliocene unit is the marine Pancho Rico Formation, consisting mainly of diatomaceous mudstone and siltstone. The Pancho Rico and the Paso Robles Formations are exposed along the east flank of the Salinas Valley from about the latitude of Greenfield to the south edge of the project area.

The phosphatic beds of the Monterey and the Pancho Rico Formations are the sources of the anomalous cadmium concentrations in the project area.

The Carmel River drainage basin is dominated by rocks of the pre-Cretaceous Sur Series, upper Cretaceous granitic intrusive rocks, and Miocene Monterey Formation.

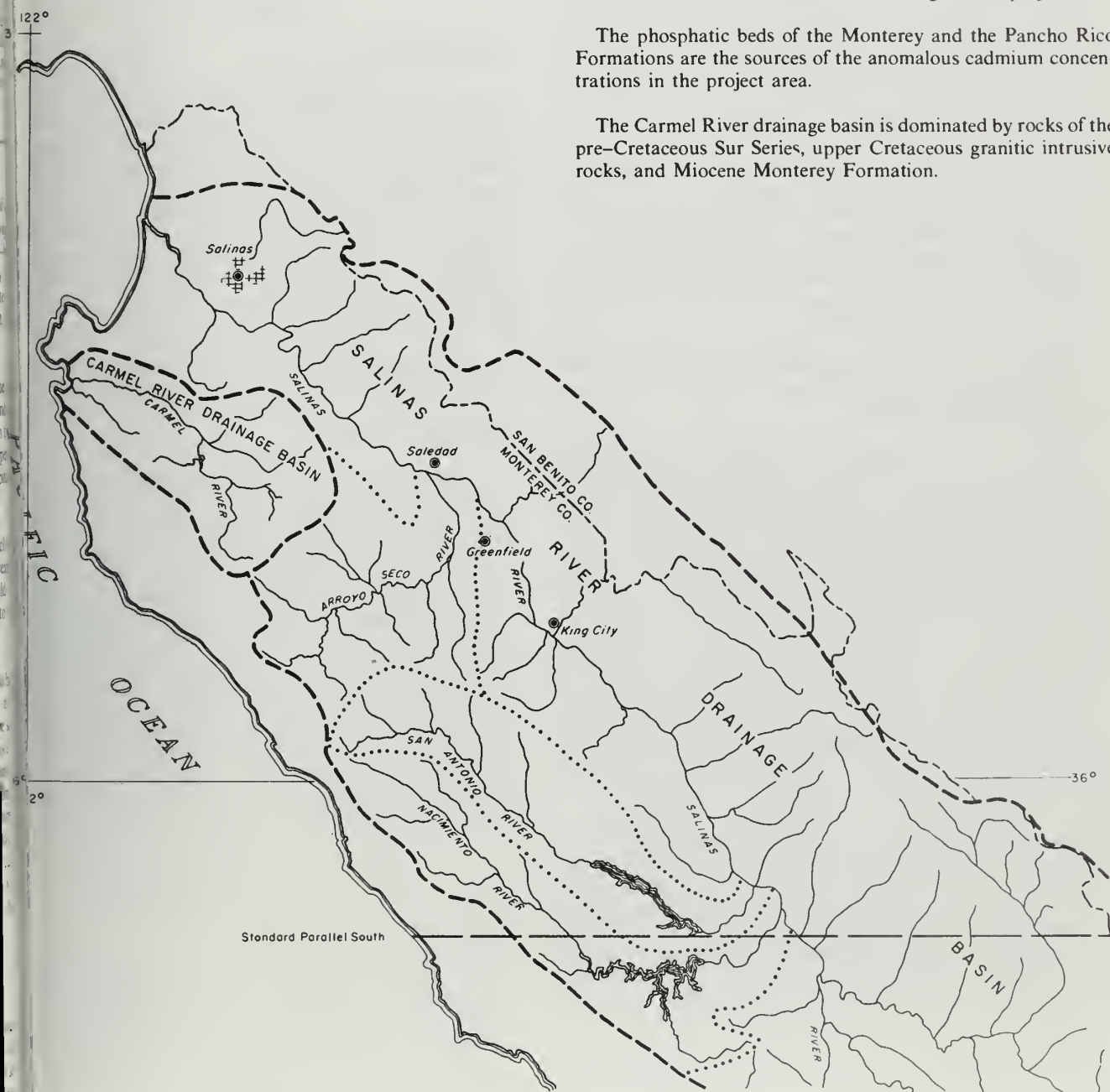


Figure 1. Index map of drainage basins in Salinas Valley.

DEVELOPMENT OF SAMPLING AND ANALYTICAL PROCEDURES

Sampling Techniques

Sampling for the first part of the project was restricted to stream sediments of the drainage basins of the Salinas and Carmel Rivers. Samples were collected from most of the streams in the area (Figure 2). A few samples were taken from ephemeral streambeds in canyons which are dry in the summer. The soil and sediment in several of the canyons have been disturbed during cultivation of barley for cattle feed, making it difficult to obtain reliable, undisturbed samples. Streams generally were found to be excellent in terms of convenience and reliability for collecting samples. A total of 201 samples of stream sediment were collected. Locations of these samples are given in Appendix A and shown on Figure 2. Locations of samples 572-576 and 593 are included on Figure 3, as they were collected south of the project area, near San Miguel and Bradley.

Sites for stream sediment sampling were spaced evenly over the project area and were selected as representative of the tributary streams. Composite samples were taken at each locality to represent the upstream drainage area. Figure 4 illustrates the pattern used: a tablespoon of the surficial sediment was collected at each of the sample points, spaced about 12½ feet apart by pacing, and put in a sample bag. Large pebbles and organic debris were discarded immediately.

Usually, 650-800 grams of sediment, representing 100 to 150 individual sample points, were collected; resulting composite sample was treated as a unit.

The size of the area sampled in this manner depended upon the local width of the stream beds, which ranged from about 20 feet to hundreds of feet. This method was devised to decrease the geochemical variability that might otherwise occur in a sample collected from a single point. The samples generally were collected from the active channel between the stream's terraces in both the wet and seasonally dry parts of the channel. Where this was not possible—for instance, in the deep water channels of the Salinas and Carmel Rivers—samples were collected from the stream deposits adjacent to the deep water. In areas under cultivation, the courses of intermittent streams could be traced by the fresh green color of the barley or grass and sampled accordingly. The sediment or, where necessary, the surface soil was collected along the trace of the stream path, and a composite sample was made.

A similar composite sampling technique was applied in collecting bedrock samples. From each rock formation, at each location, rock chips were collected at intervals of one to two feet over the entire exposure. A composite sample was made by crushing all of the chips. Thus, each composite sample provided a representative sample of the exposed portion of each formation. A total of 259 composite bedrock samples were collected. (Figure 3 and Appendix B). At some locations, samples were collected from a depth as great as two feet, as well as from the surface, in order to check the vertical variability.

Computer programs (Appendix I) were used for preparation of the sample identification list, tables of chemical analyses, and for storage and retrieval of chemical analyses.

Sample Preparation

The organic contents of each stream sediment sample, such as dried leaves, grass, bark, rootlets, and other foreign objects, removed by handpicking, using a magnifying lens. Wet samples were dried under infrared heat lamps; all other samples air-dried. After the samples were sieved and all material finer than 18-mesh was discarded, the minus 18-mesh fraction split (using a Jones splitter) until a representative portion of 120-130 grams was obtained. This was pulverized (using a Braun pulverizer) and used for chemical analysis.

Bedrock samples were similarly crushed, pulverized, and used for chemical analysis.

Digestion

STREAM SEDIMENT SAMPLES

Two separate digestion techniques were employed for stream sediment samples: one for arsenic, cadmium, copper, lead, mercury and zinc; the other especially for cadmium. Samples containing less than 2.5 ppm Cd could not be determined and were digested by the total digestion technique which requires a dilution factor of 25, while the detection limit for Cd is 0.1 ppb solution. This would make it impossible to detect the very low concentrations of cadmium present in some of the samples. Therefore, a special digestion technique was used on the portion of the split to be analyzed for cadmium. Both techniques are described in detail in Appendix D.

For the minimum concentrations of element that can be determined, see footnotes under Appendices F and G.

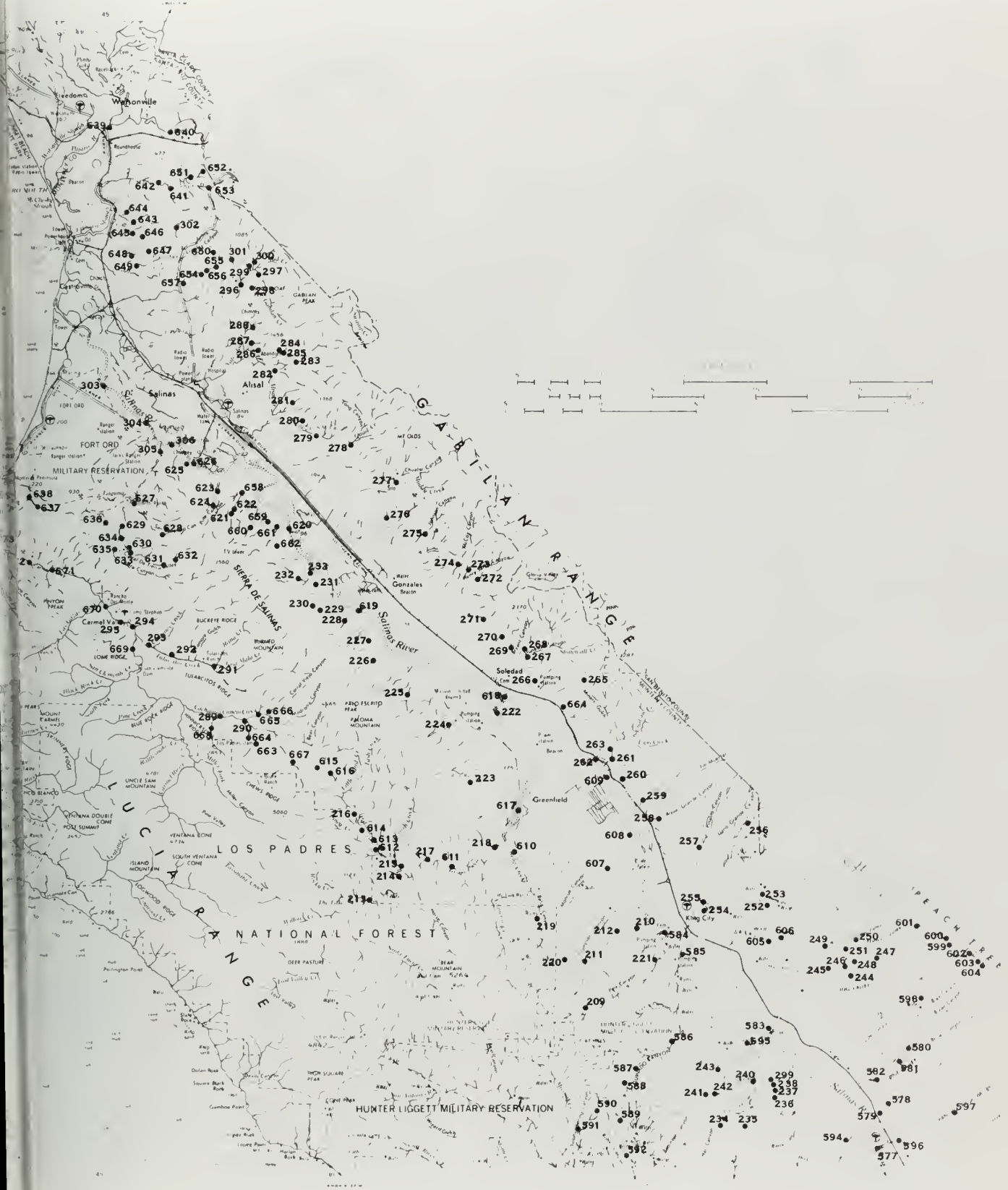
BEDROCK SAMPLES

Bedrock samples with a high concentration of phosphorus presented a special problem when digested by the total digestion technique. A white complex compound was produced which adhered to the glass walls of the apparatus and could not be removed easily, particularly from the inaccessible, thin, and narrow closed tube of the modified soxhlet extractor. The compound would sublime when heated but would condense on the same wall when cooled. Because of this contamination problem the extractor could not be reused, so another digestion technique was developed (see Appendix D). Also, there was some doubt as to whether or not the cadmium salts from the bedrock samples were completely dissolved by use of the cold acid extraction technique, which worked so satisfactorily for the stream sediments. Thus, various techniques were developed and used to digest bedrock samples. Details of these techniques are given in Appendix D.

Analytical Techniques

MERCURY

For purposes of pollution control or toxicity monitoring, many analytical techniques are used to analyze for mercury in various types of samples. Atomic absorption spectrophotometry is excellent for use in trace element determination, but the technique lacks the sensitivity to measure mercury in the parts-per-billion range. The flameless technique of atomic absorption spectroscopy used here, which gave a detection limit of 0.1 ppb Hg,



Index map of locations of stream sediment samples, Salinas Valley.

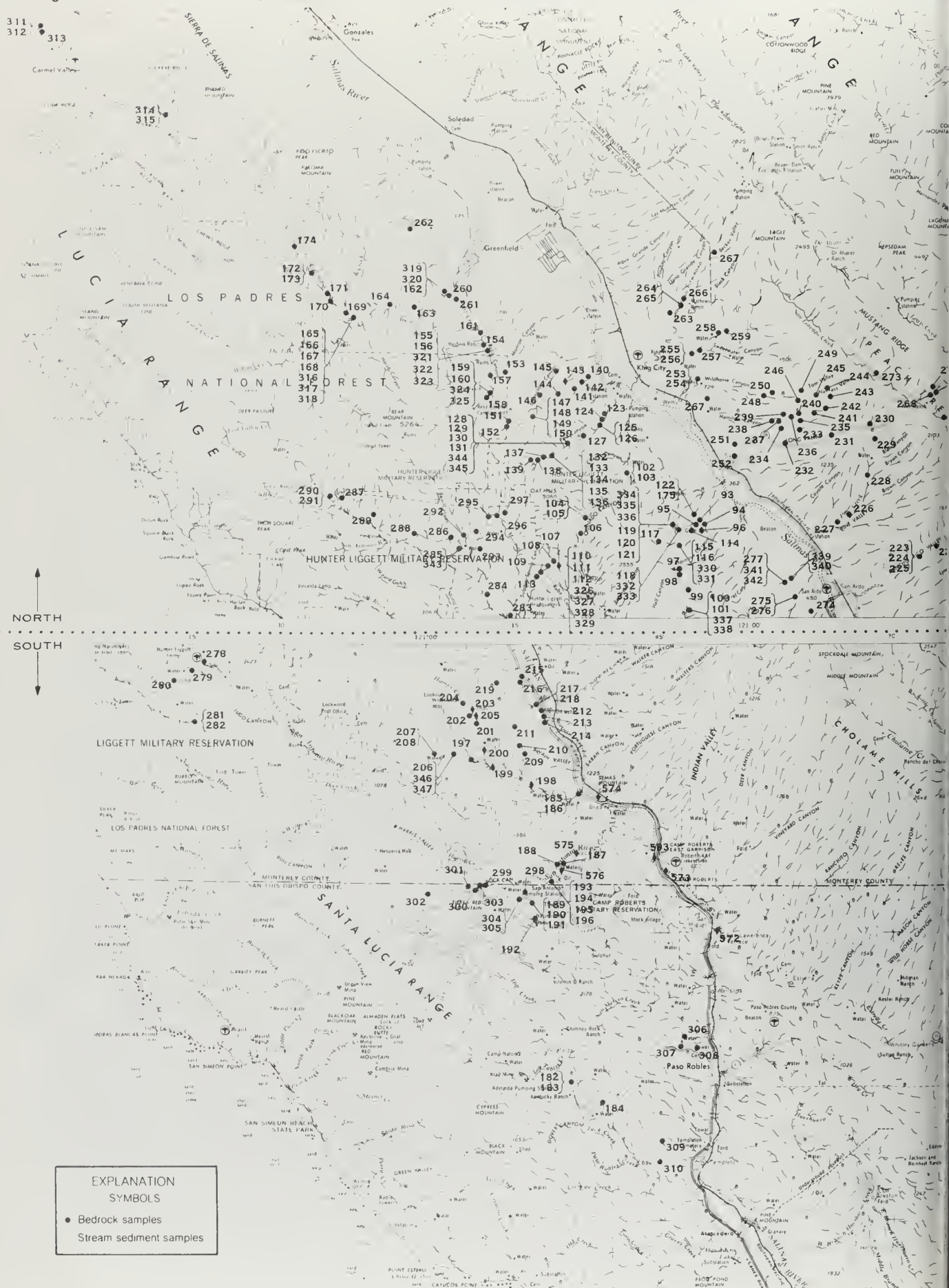


Figure 3. Index map of locations of bedrock and some stream sediment samples from Solinos Volley.

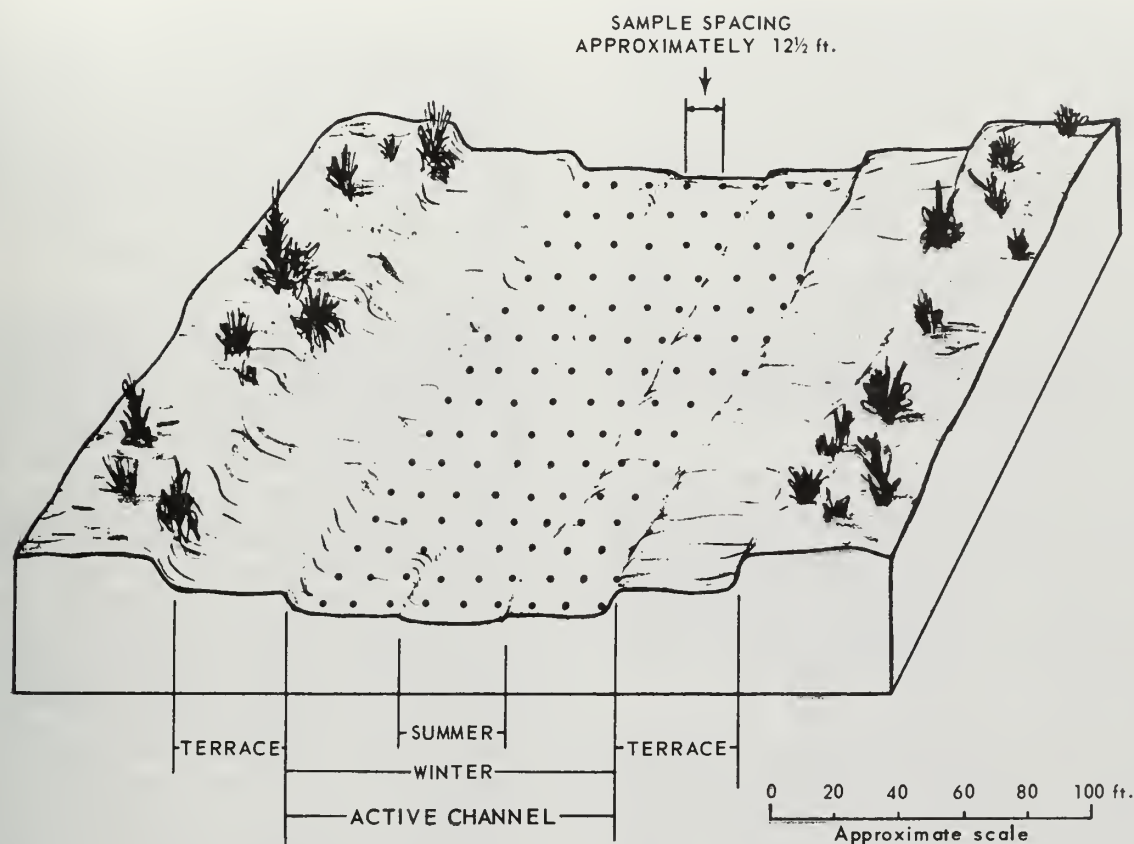


Figure 4. Technique for collecting composite stream sediments samples.

The mercury salts in digested samples were reduced to elemental mercury by the addition of stannous chloride to the sample solution in a reaction vessel equipped with a magnetic stirrer. The mercury vapor thus released was transported by diffusion through a drying column to an absorption cell. The absorption cell replaced the conventional burner in the optical path of the atomic absorption spectrophotometer. The absorption was measured at the 2537 Å Hg wavelength and plotted on a chart recorder. Mercury standards were measured and recorded similarly. The concentration of mercury in the samples was determined by relating the peak heights of those of the standards. Details of this technique are described in Appendix E.

ARSENIC

Arsenic presents certain analytical problems which make its determination difficult. The commonly used air-acetylene flame cannot be used because arsenic resonance lines lie in the far ultraviolet region, where flame absorption is a problem. With an air flame, which creates a high background, there is a strong light absorption and the available energy striking and photomultiplier is reduced. If an argon-hydrogen flame is used instead of an air-acetylene flame, these problems are considerably reduced. A danger of the argon-hydrogen flame is that it is colorless and an operator may touch the burner when the unit is in operation.

In the technique used, arsine gas was produced by reduction of stannous hydrogen generated by the addition of zinc to hydrochloric

acid. This arsine gas was collected in a rubber balloon, along with excess hydrogen and hydrogen sulfide gas if sulfide minerals were present in the sample. The arsine gas was carried away and introduced into the flame by means of an argon carrier gas. This technique gave very good sensitivity, allowing the detection of arsenic at submicrogram levels. By releasing the original sample matrix, interelemental interferences in the flame also were minimized.

The sample digests which were used for mercury determination also were used for arsenic determination after removing the suspended particles by filtering. The only difficulty with these digests is that they contain a considerable amount of nitric acid, which prevents the production of arsine. Nitric acid was, therefore, completely removed from these sample digests by slowly heating them with concentrated sulfuric acid.

Details of the adopted procedure are given in Appendix E.

CADMIUM, COPPER, LEAD, AND ZINC

Cadmium, copper, lead and zinc were determined by routine atomic absorption analytical procedures by direct aspiration of the sample digests.

PHOSPHORUS

Phosphorus was determined with the x-ray spectrometer by mixing one gram of 230-mesh sample with one gram of What-

man CF-11 cellulose powder, making pellets in Spex caps, and analyzing with an EDDT crystal and Cr target x-ray tube (Appendix E). All phosphorus results are corrected for the presence of high calcium.

RESULTS OF ANALYSES

Mercury

The general level of mercury in both stream sediments and bedrocks is lower than Taylor (1964) reports in the earth's crust (80 parts per billion); in bedrock samples, however, its level is about the same as in soils.

Only six stream sediment samples contained anomalous amounts (> 65 ppb Hg) of mercury. The largest mercury concentration was 512 ppb Hg in Thompson Canyon, apparently from middle Miocene Monterey rocks. Five other samples contained 75–88 ppb Hg; three from streams draining an area of Pleistocene nonmarine sediments, and two from San Lorenzo Creek, which drains an area of Middle and/or Lower Pliocene marine sedimentary rocks and Holocene alluvium.

The threshold level—the transition point between normal (lognormal, here) and anomalous concentration—of mercury is 64.5 ppb Hg in stream sediment samples and 50 ppb Hg in bedrock samples. The cumulative frequency distribution for mercury for stream sediments is lognormal, while the bedrock samples show the presence of two separate populations with the anomalous population being 35 percent of the total analyzed samples.

Arsenic

Arsenic in the stream sediments seems to be at levels generally found in the earth's crust (Taylor, 1964), but lower than levels generally found in soils (Vinogradov, 1959). Arsenic appears to be present in the bedrocks at considerably higher levels than generally found in crustal rocks, but at approximately the same levels generally found in soils. The threshold levels of arsenic in the stream sediments is 9.25 ppm, and only three samples (1.5 percent of total collected samples) exceed this upper limit. From their locations near the south end of the project area, these three samples seem to have been derived from the rocks of the Middle Miocene marine Monterey Formation. In general, the samples collected from the southeast portion of the project area (the source apparently being the same rocks) show higher concentrations of arsenic than the samples collected from other parts of the area.

The threshold levels of arsenic in bedrocks is 38 ppm, and only eight samples (three percent of total collected samples) appear to exceed this upper limit. The distribution seems to be lognormal in both stream sediments and bedrocks. Samples of clay seams have unusually high amounts of arsenic.

In the project area, arsenic compounds are used as a chicken feed supplement to increase their growth rate, and chicken droppings are widely used as a fertilizer. No connection was established in this study between this possible source of arsenic and the anomalous arsenic values. Overall, arsenic is not abundant enough to be a health hazard in the project area.

Cadmium

In Monterey County, some stream sediment samples show higher concentrations of cadmium than the general world-concentration in the crust (0.2 ppm; Taylor, 1964) or in the (0.5 ppm; Vinogradov, 1959). In general, the stream sediment samples collected from southwest and southeast of King and San Ardo contain anomalously large amounts (1.5 ppm; cadmium). Stream sediment samples from that same area are high in arsenic and zinc. The source of these sediments apparently is the Middle Miocene marine rocks.

The California Department of Agriculture and the University of California at Davis, Department of Environmental Toxicology ran a special sampling program in the Greenfield–King and San Ardo area to determine the cadmium contents of agricultural soils and the plants growing on them. Their results, 140 collected samples, show that Lockwood Loam soil, as well as the vegetation associated with it, contains greater amount of cadmium than other soils and their associated vegetation. Spinach and other leafy vegetables appear to carry higher cadmium contents than citrus fruits; grapes, in particular, contained normal amounts of cadmium. Lockwood Loam soil has been formed from older alluvial fans derived from the same general vicinity in the southeast part of the project area in which sediments show high concentrations of cadmium. The results of the study conducted by California Division of Mines and Geology personnel therefore, correlate positively with results of studies made by personnel of the California Department of Agriculture and University of California at Davis Department of Environmental Toxicology. In addition to surface samples, the Department of Environmental Toxicology took several cores of agricultural soils from this area to depths of six feet, and found that cadmium concentration is generally high and uniform throughout the foot depth. This indicates that cadmium's presence is not due to the addition of fertilizer to the surface soils.

The background calculated for a perfect frequency distribution curve corresponds to the mode and median values and is the geometric mean of the results (Lepeltier, 1969). This geometric mean is a more significant value than the arithmetic mean, also a more stable statistic, and less subject to change with addition of new data and less affected by high values. The results for cadmium in bedrocks illustrate this. A high concentration of cadmium in some of the bedrock samples produces the arithmetic mean of 27.2 ppm Cd, which is higher than the threshold of 15 ppm Cd. The geometric mean, however, which is 5.2 ppm Cd, is not affected by the very high cadmium content of some of the samples. The concentrations of cadmium in bedrock samples is higher than crustal or soil abundances (Taylor, 1964; Vinogradov, 1959). A total of sixty-three samples (24 percent of all samples collected) exceed the threshold level. The cumulative frequency distribution for cadmium shows the presence of two distinct populations, one normal and the other positive and anomalous. It also shows a positive skew in the direction of higher values.

Lead

The geometric mean of lead content of all stream sediment samples is 7.9 ppm, which is less than the values reported by Taylor (1964) for crustal abundance (12.5 ppm), or by Vinogradov (1959) for its abundance in soil (10.0 ppm). Lead levels seem to be higher in bedrock samples than generally found in the crust or soil. The threshold levels of lead in stream sediments and bedrocks are 29.0 ppm and 33.0 ppm Pb, respectively, and

ms to be distributed at random throughout the project area. sediment sample from the Salinas River near San Ardo con- ned 102 ppm Pb, and five other stream sediment samples, mostly from Elkhorn Slough drainage, contained anomalous ounts of lead ranging from 38 to 53 ppm. The cumulative uency distribution for lead in bedrock samples is primarily mal, with only one percent of the population being anoma- s.

Copper and Zinc

The combined total of these elements in the sediments yzed was lower than the world-wide average in the crust (Cu 0.0, Zn 70.0 ppm; Taylor, 1964), or in the soil (Cu 20.0, Zn 50.0 n; Vinogradov, 1959). The King City-San Ardo area shows h levels of arsenic and cadmium as well as high levels of per and zinc.

The general levels of copper and zinc in bedrock samples seem e lower than those in most crustal rocks, but about the same n soils.

The threshold level for copper is 13.0 ppm in stream sediments 40.0 ppm in bedrocks. For zinc, the threshold level is 74.0 n in stream sediments and 250.0 ppm in bedrocks. Thirty- ee stream sediment samples contained more copper than the hreshold level; nine samples contained more zinc. The source of e element for most of these samples was the Middle Miocene nine Formation.

The cumulative frequency distribution for copper in both am sediments and bedrocks shows the presence of two popu- ons, one normal, the other anomalous. The cumulative fre- uency distribution for zinc in both stream sediments and edrocks shows lognormal distribution.

Phosphorus

only the bedrock samples having more than 10 ppm Cd were yzed for phosphorus. The level of phosphorus seems to be siderably higher than soil and crustal abundances reported y Taylor (1964) and Vinogradov (1959) respectively. The hreshold level is 1.0% P. The cumulative frequency distribution of phosphorus shows the presence of two separate populations; 5 percent of the total analyzed samples constitute the anoma- or population.

from this analytical data, single element distribution maps for o stream sediments and bedrocks were prepared for each e element (Figures 5 through 17).

CORRELATION

The results of the analyses of the stream sediment and bedrock mples were processed by means of a stepwise regression com- ut program devised by Health Sciences Computing Facility C.L.A. Comparisons between concentrations of all elements estd were made in pairs, using regression analysis, in an effort arn which elements tend to be associated in the materials estd.

Atabular summary of the correlation matrices, arranged in ai of elements used in the computation, is presented in Tables

3 and 4. Any correlation higher than 0.5000 is higher than 50:50 average; correlation higher than 0.7000 are considered mean- ingful in the present study. For the stream sediment samples, six pairs of elements (As-Cd, As-Cu, As-Zn, Cd-Cu, Cd-Zn, and Cu-Zn) show significant correlations (Figures 18 through 23): if one element in a pair is high in a sample, the other tends also to be high; however, it is not possible to predict the quantity of the other element by analyzing only one element in each pair.

Table 3. Correlation matrix (stream sediments).

As	Cd	Cu	Pb	Hg	Zn	
1.000	0.8724	0.7732	0.1859	0.2892	0.7875	As
	1.0000	0.7558	0.0527	0.2414	0.8326	Cd
		1.0000	0.3692	0.4425	0.8816	Cu
			1.0000	0.1994	0.2219	Pb
				1.0000	0.4088	Hg
					1.0000	Zn

Table 4. Correlation matrix (bedrocks).

As	Cd	Cu	Pb	Hg	P	Zn	
1.0000	0.4129	0.4698	0.4502	0.1931	0.3224	0.5278	As
	1.0000	0.7548	0.2699	0.2532	0.9492	0.9123	Cd
		1.0000	0.3189	0.1615	0.8409	0.9020	Cu
			1.0000	0.1059	0.2199	0.3803	Pb
				1.0000	0.3710	0.2060	Hg
					1.0000	0.9478	P
						1.000	Zn

An attempt was made to correlate the analytical results of stream sediment chemistry with the geology of the area to deter- mine which bedrock units were parents of the anomalously high values of each tested element. This correlation of stream sedi- ment chemistry with the geology of the area was inferential at best, because some of the samples had accumulated from a num- ber of possible parent rocks, and at that stage no analyses had been made to determine which bedrock formations have concen- trations of one or more of the elements tested. A transparent copy of the stream sediment sample locations map was posi- tioned over the geological map of Monterey County (Hart, 1966), and the possible sources of each sediment then were determined in terms of geological formations exposed in the drainage basins. Wherever there was doubt, the two most likely sources were considered. The stream sediment samples collected from the Salinas and Carmel Rivers and from the Arroyo Seco were not used in this correlation, because they were transported from long distances and represent a heterogeneous mixture of sediments received from many geological formations. The scope of this first stage of the project did not include the testing of individual geological units.

Table 5 lists the range and average amounts of the six elements in stream sediment samples derived from the various geological formations in the project area.

Among the bedrock samples, six pairs of elements (Cd-Cu, Cd-P, Cd-Zn, Cu-Zn, P-Cu, and P-Zn) show significant as- sociations (Figure 24 through 29). Samples belonging to phos- phatic beds appeared to have high-cadmium contents. In fact, almost all phosphatic rocks in the area have high cadmium contents except eleven samples which have high cadmium but low phosphorus. Four samples have free-sulfur encrustations that probably resulted from sublimation of sulfide solutions. All

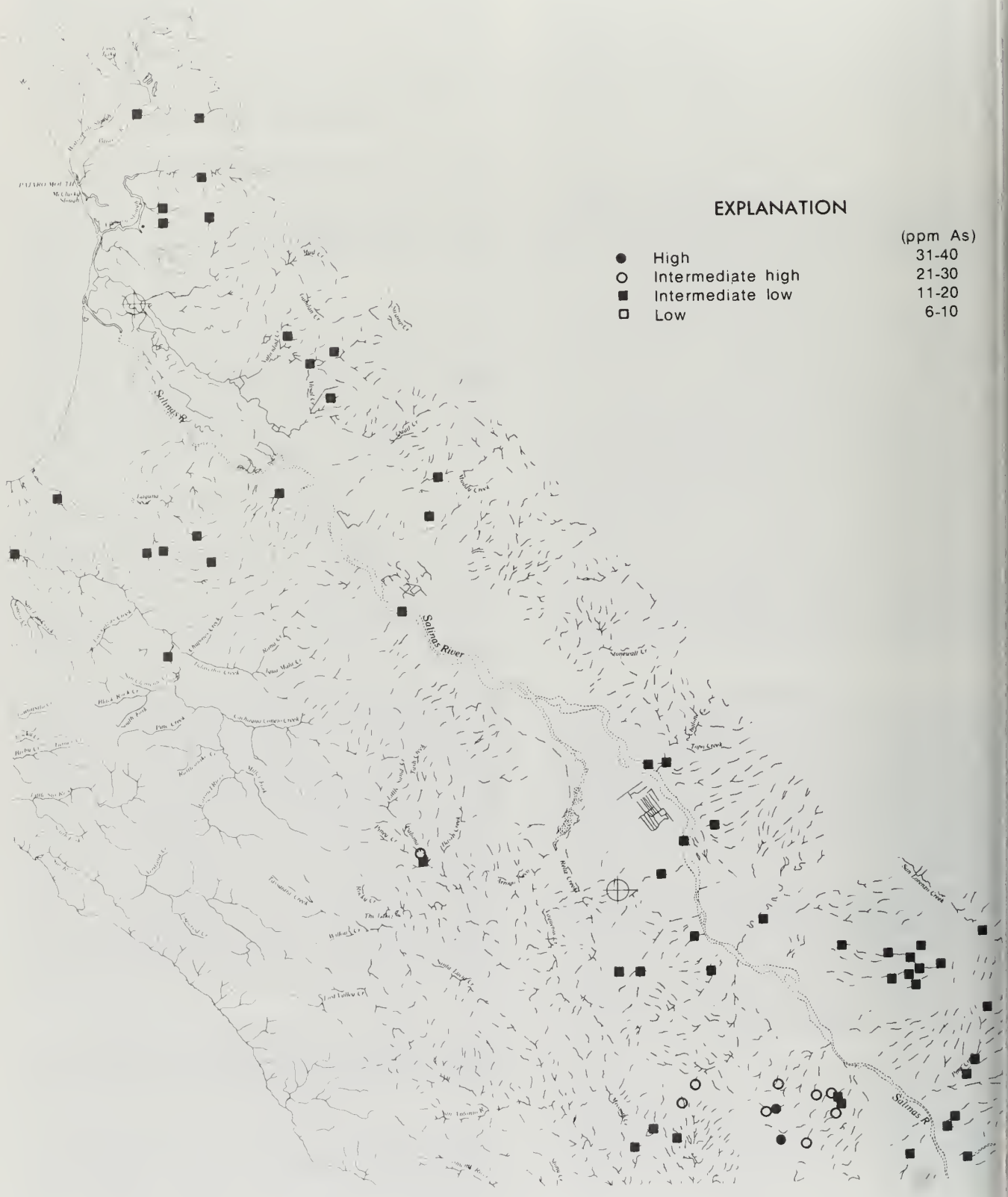


Figure 5. Map showing arsenic in stream sediments.

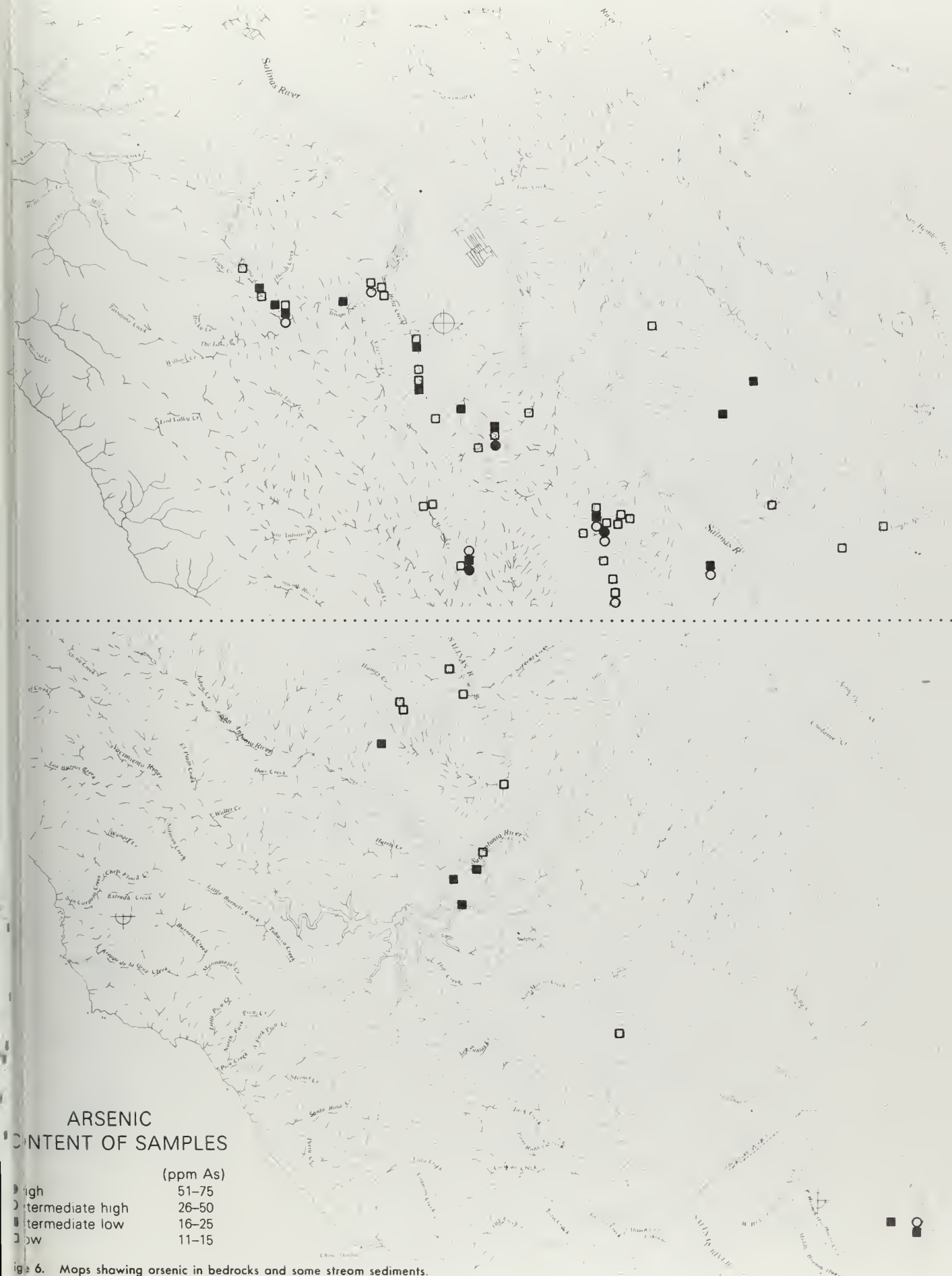


Fig. 6. Maps showing arsenic in bedrocks and some stream sediments.

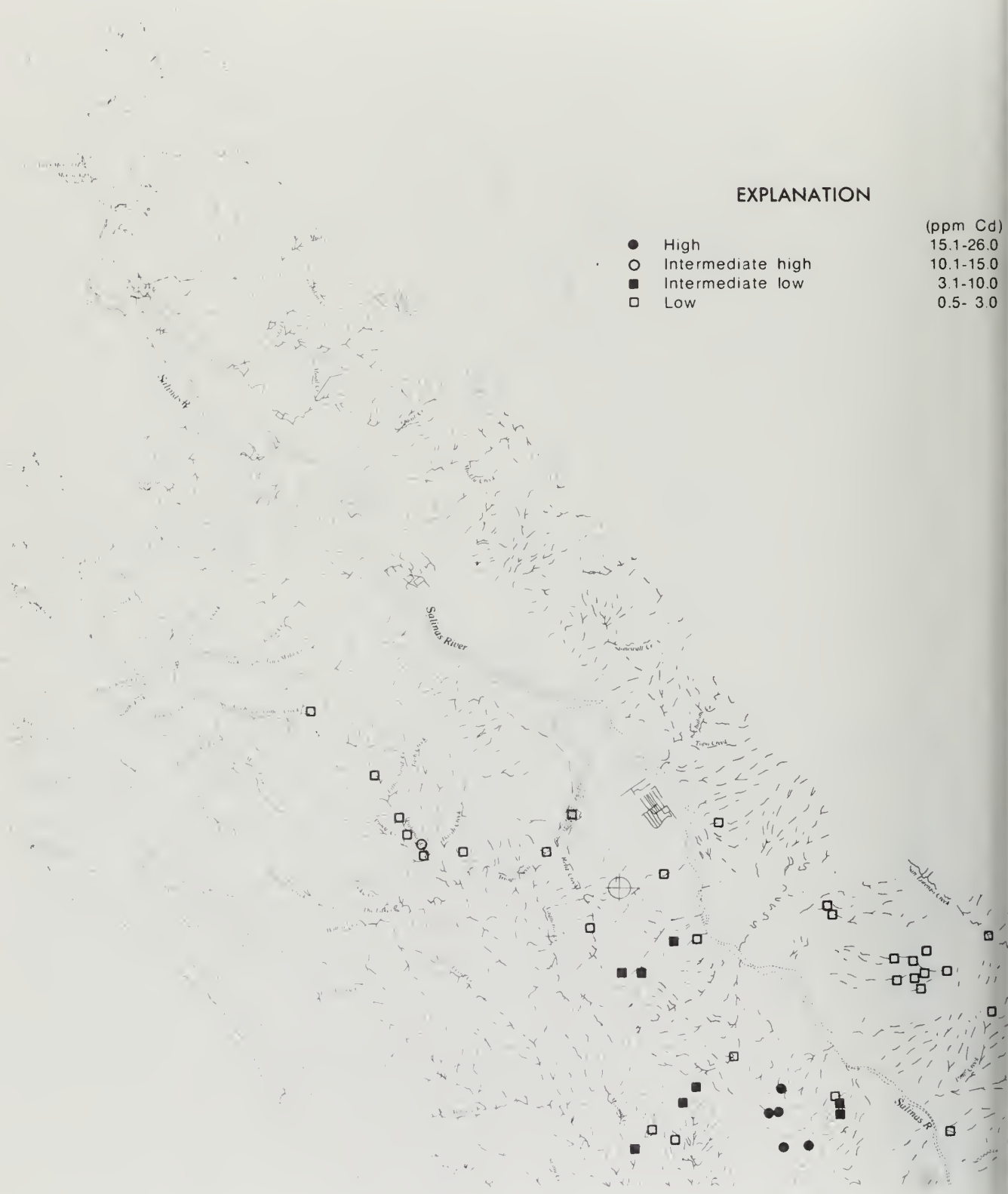


Figure 7. Map showing cadmium in stream sediments.

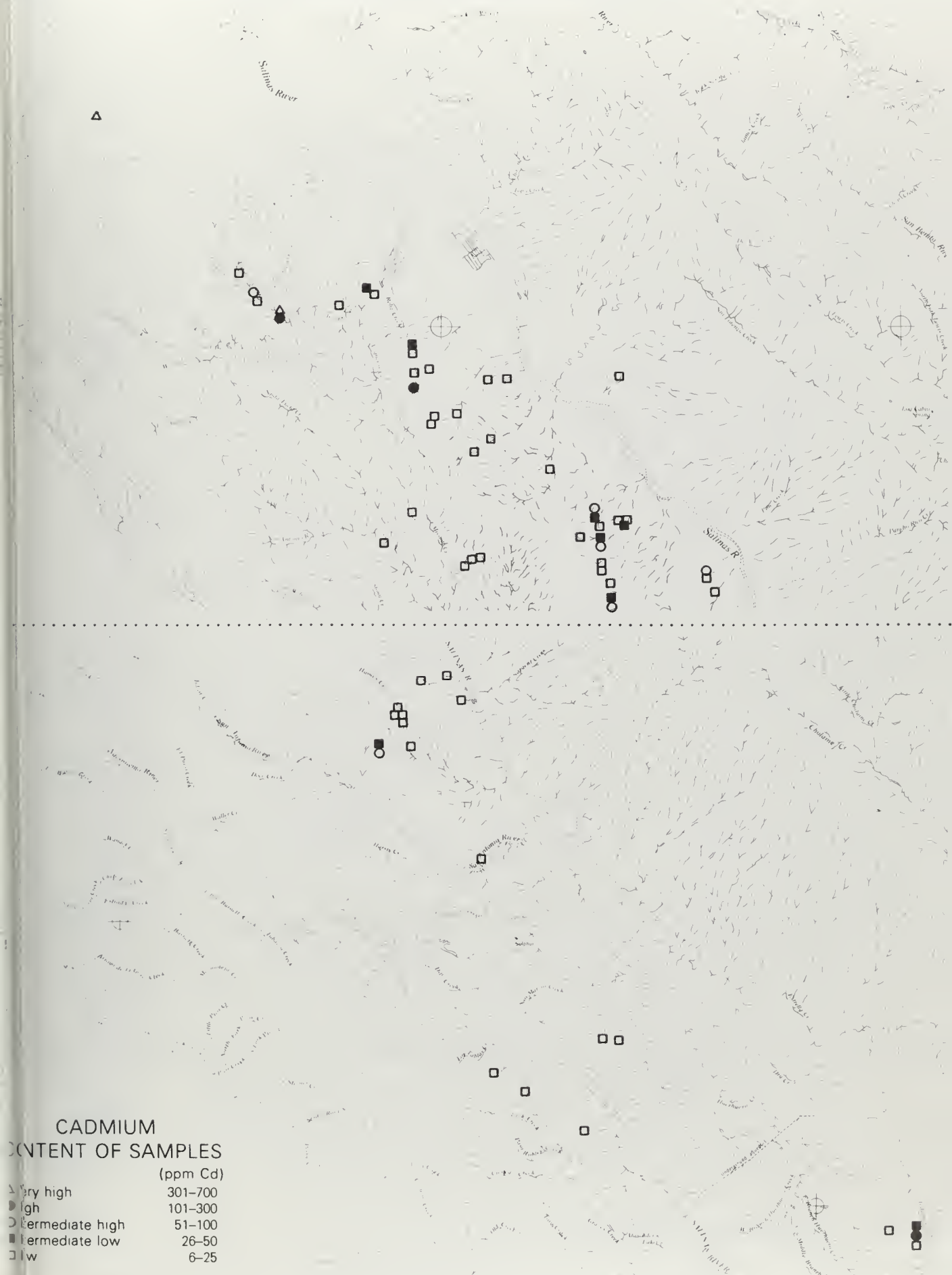


Fig. 8. Maps showing cadmium in bedrocks and some stream sediments.

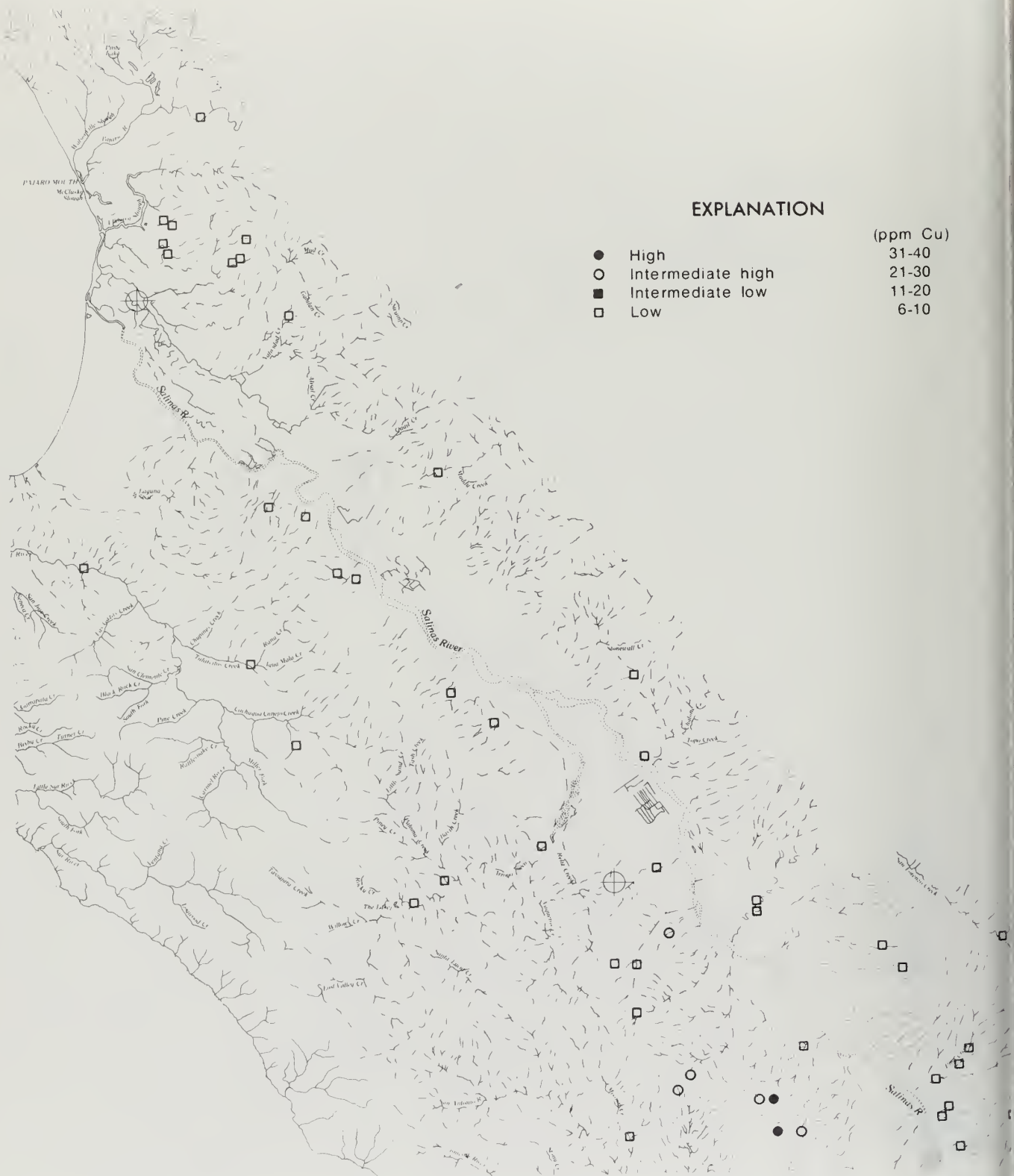
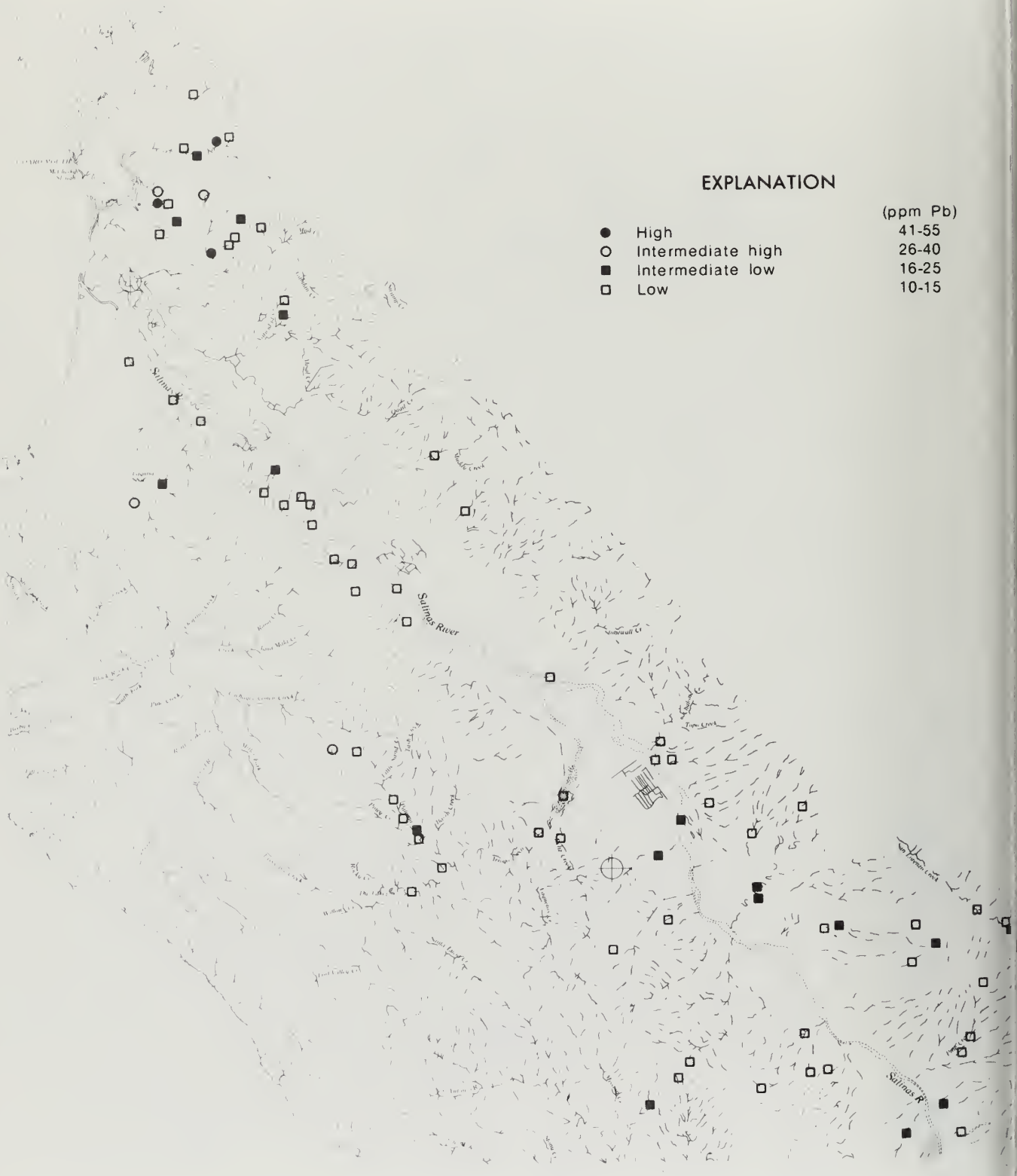


Figure 9. Map showing copper in stream sediments.



Fig. 10. Maps showing copper in bedrocks and some stream sediments.



EXPLANATION

●	High	(ppm Pb)	41-55
○	Intermediate high		26-40
■	Intermediate low		16-25
□	Low		10-15

Figure 11. Map showing lead in stream sediments.



Figure 12. Maps showing lead in bedrocks and some stream sediments.

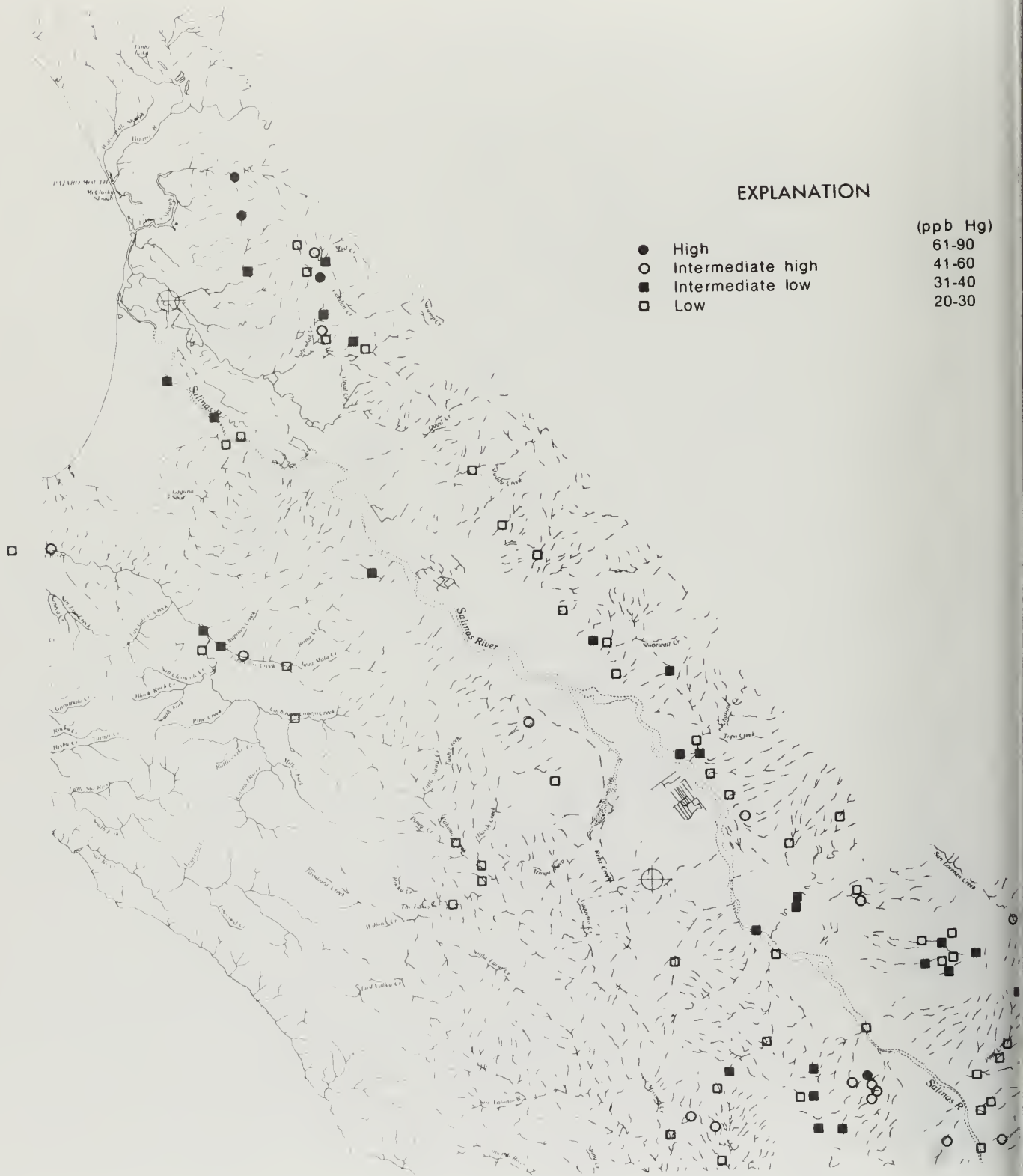


Figure 13. Map showing mercury in steam sediments.

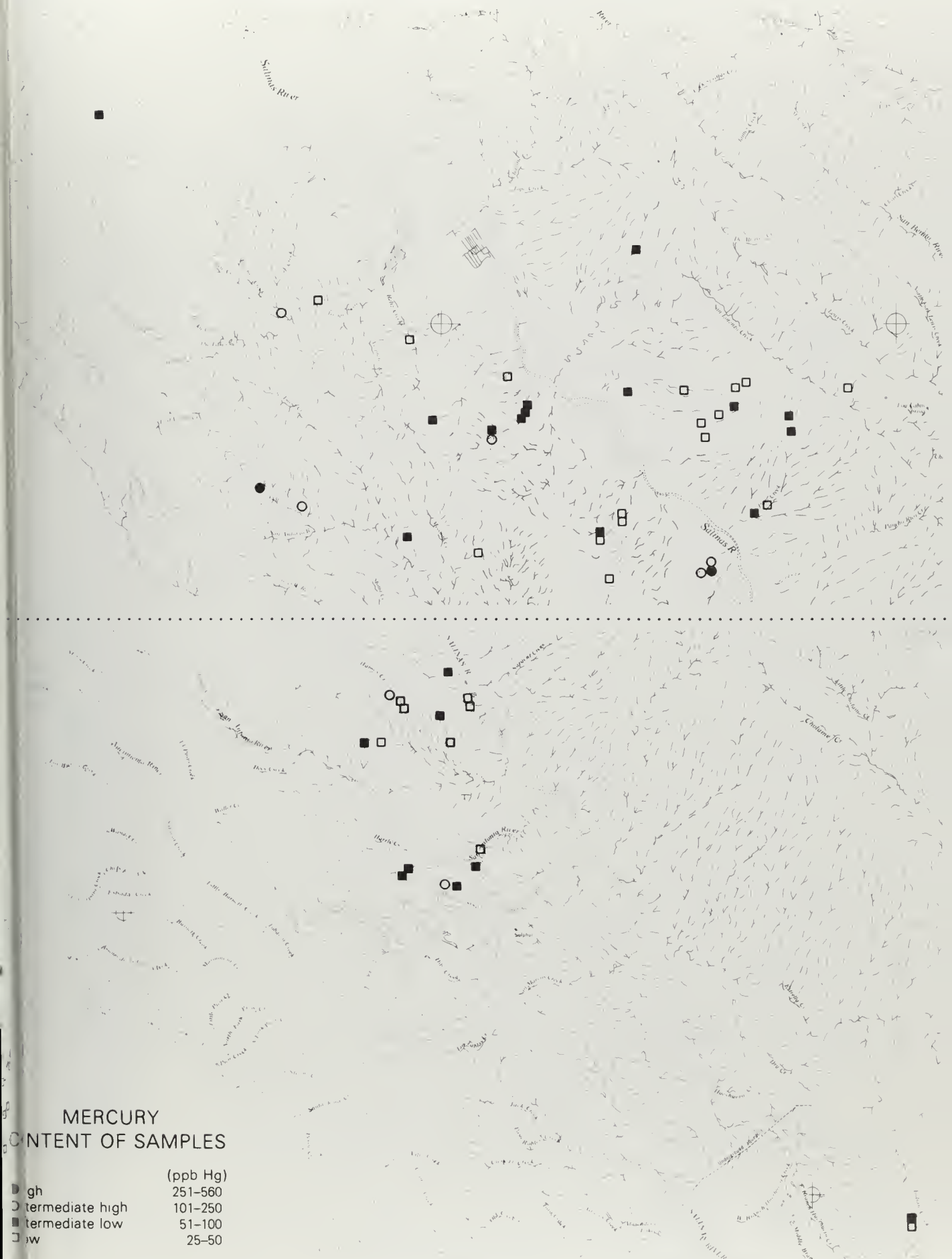


fig. 14. Maps showing mercury in bedrocks and some stream sediments.

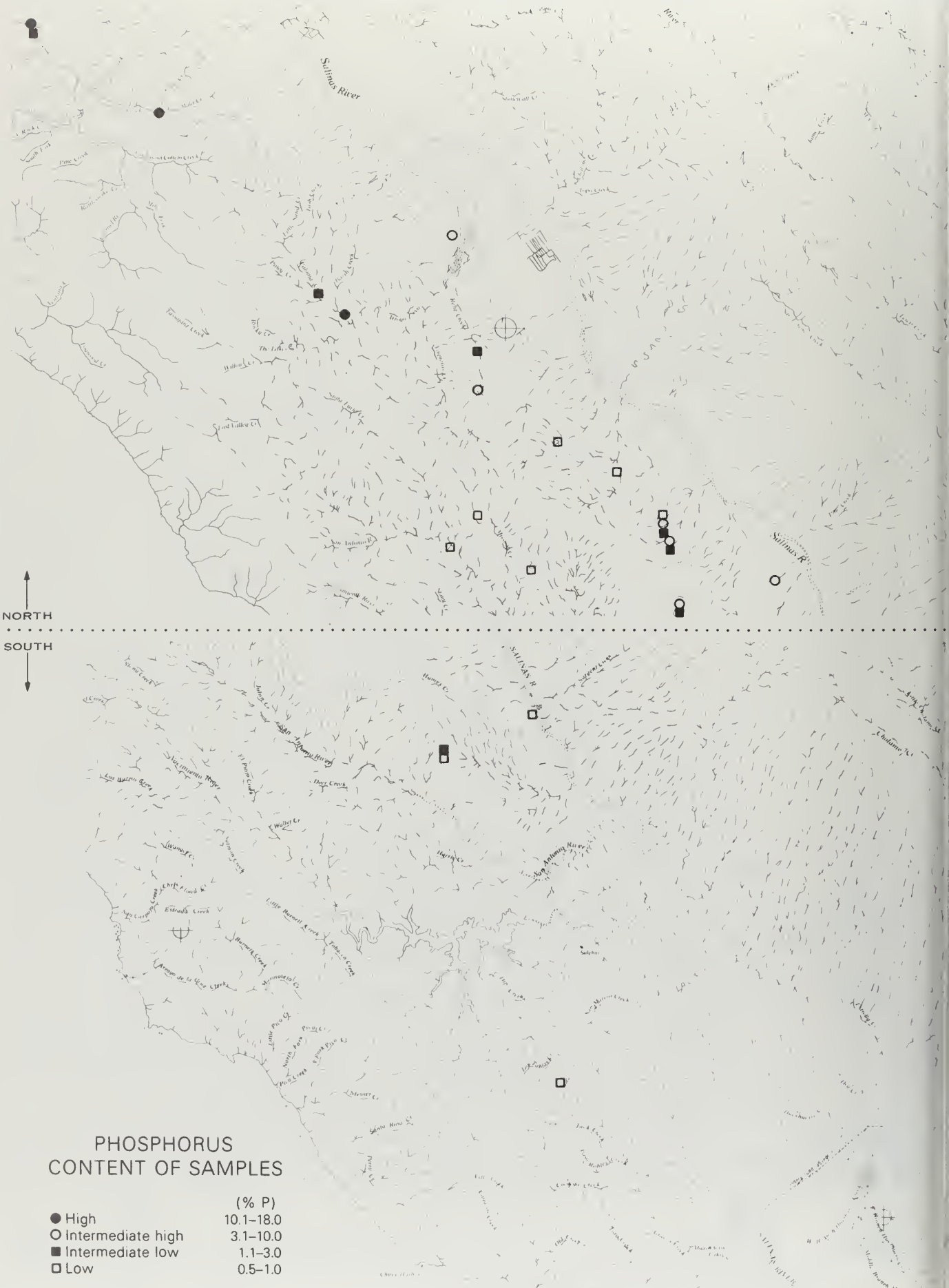


Figure 15. Maps showing phosphorus in bedrocks and some stream sediments.

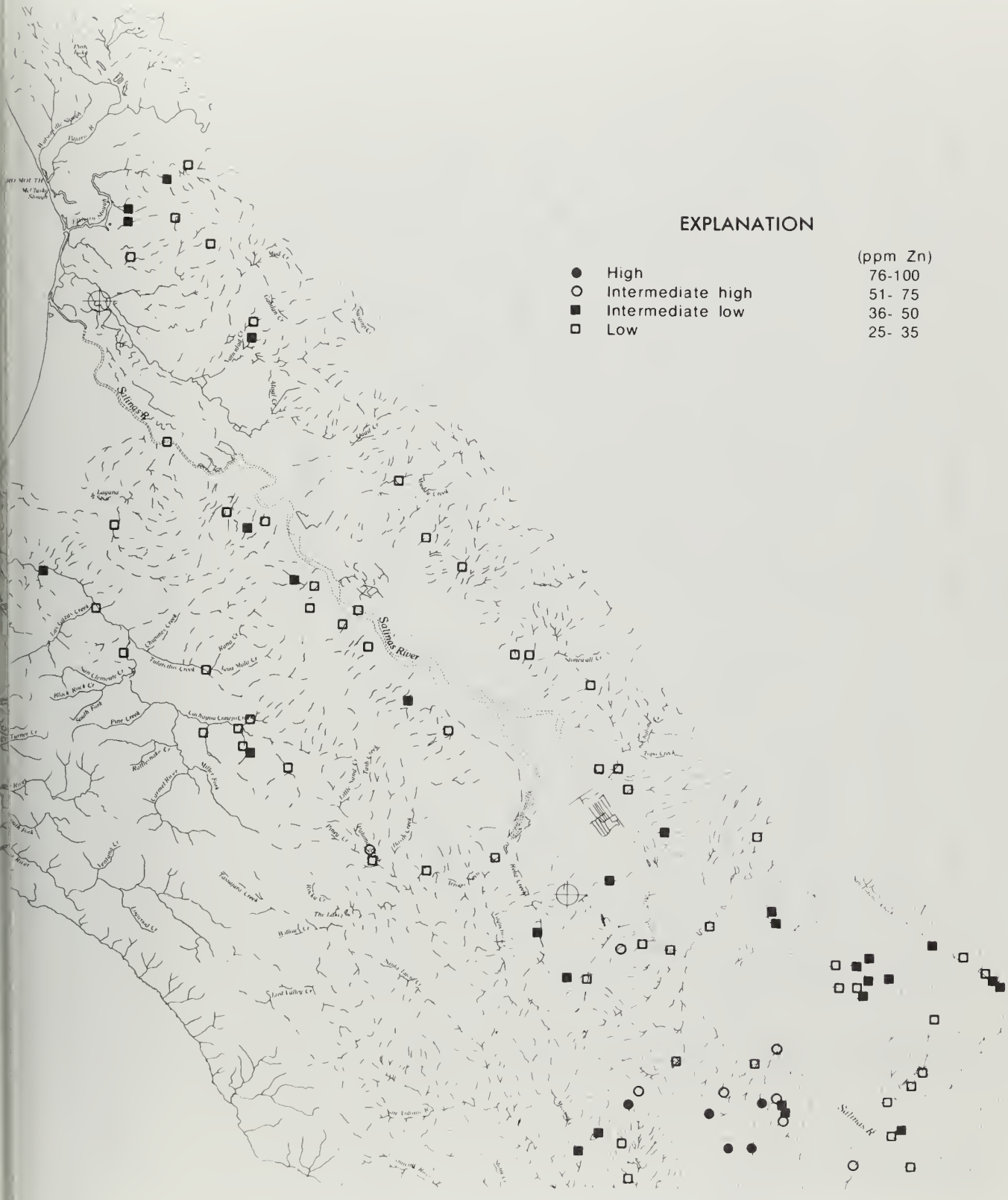


Figure 16. Map showing zinc in stream sediments.

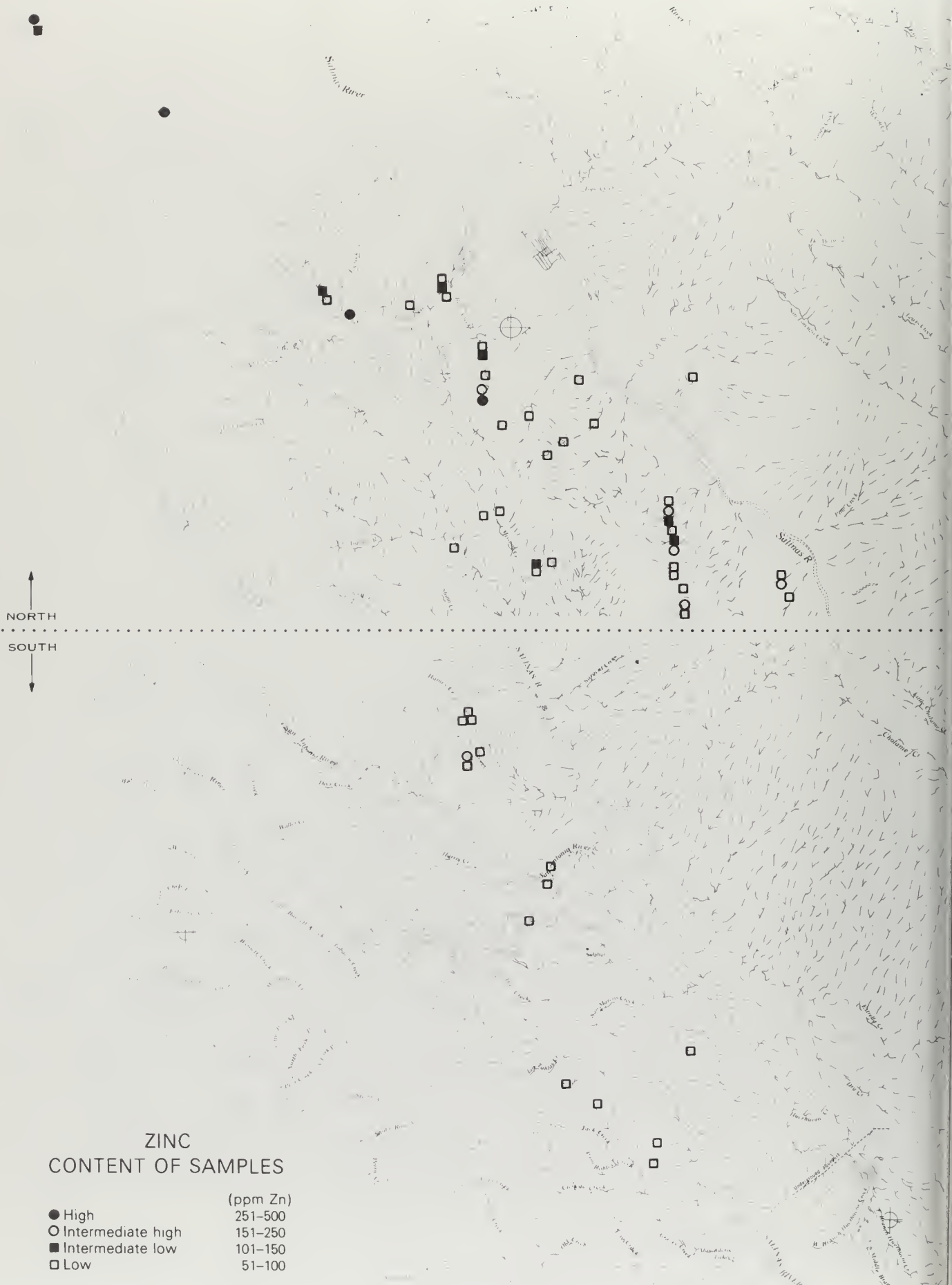


Figure 17. Maps showing zinc in bedrocks and some stream sediments.

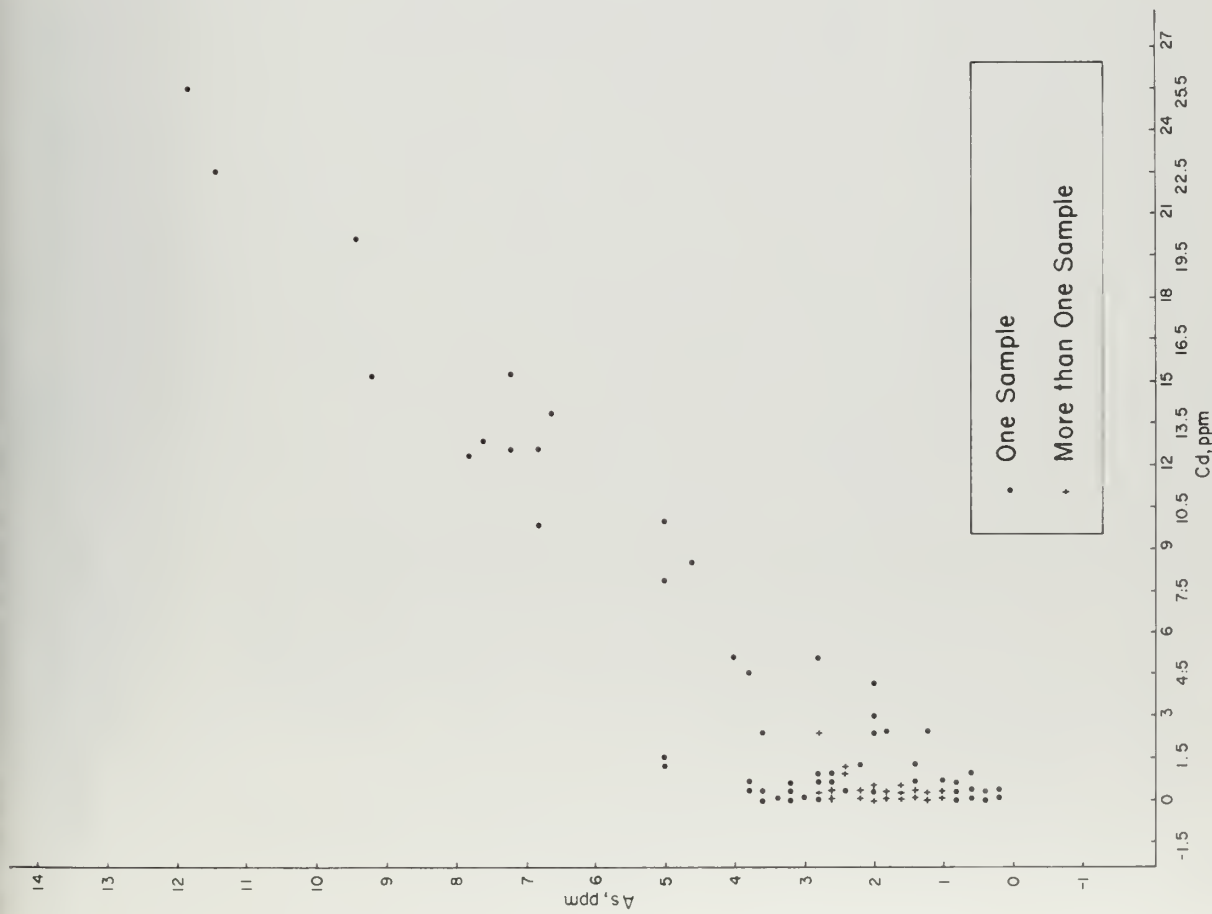


Figure 18. Correlation between arsenic and cadmium in stream sediments.

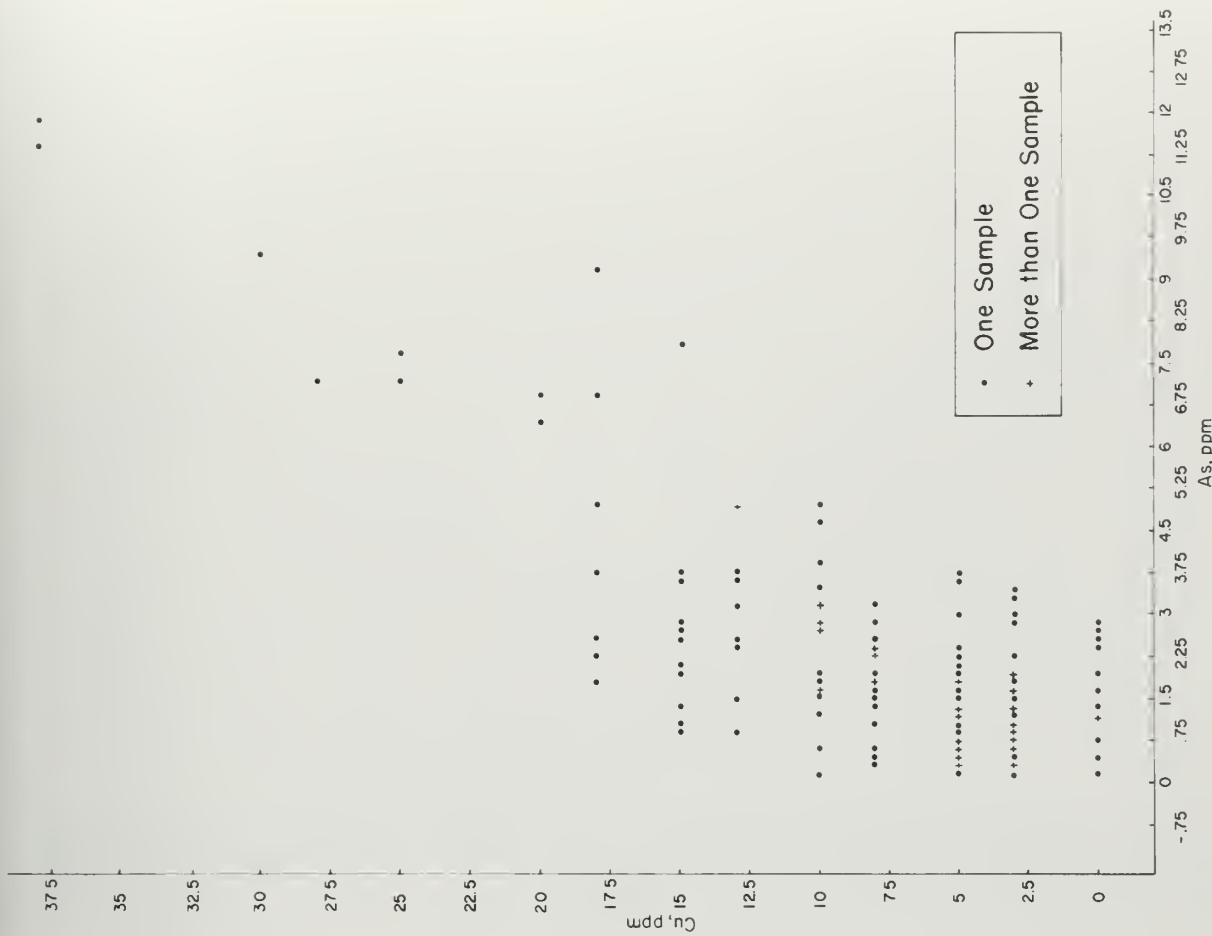


Figure 19. Correlation between arsenic and copper in stream sediments.

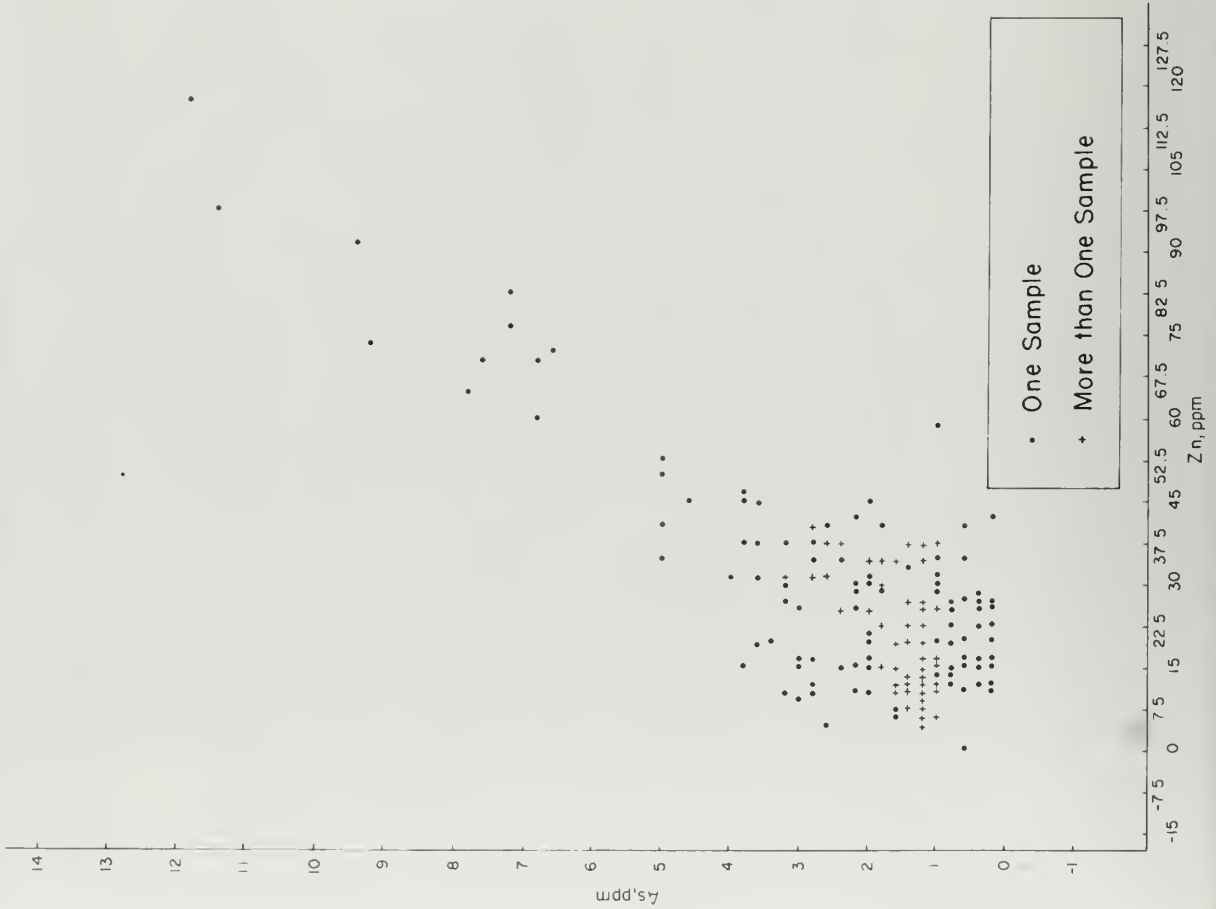


Figure 20. Correlation between arsenic and zinc in stream sediments.

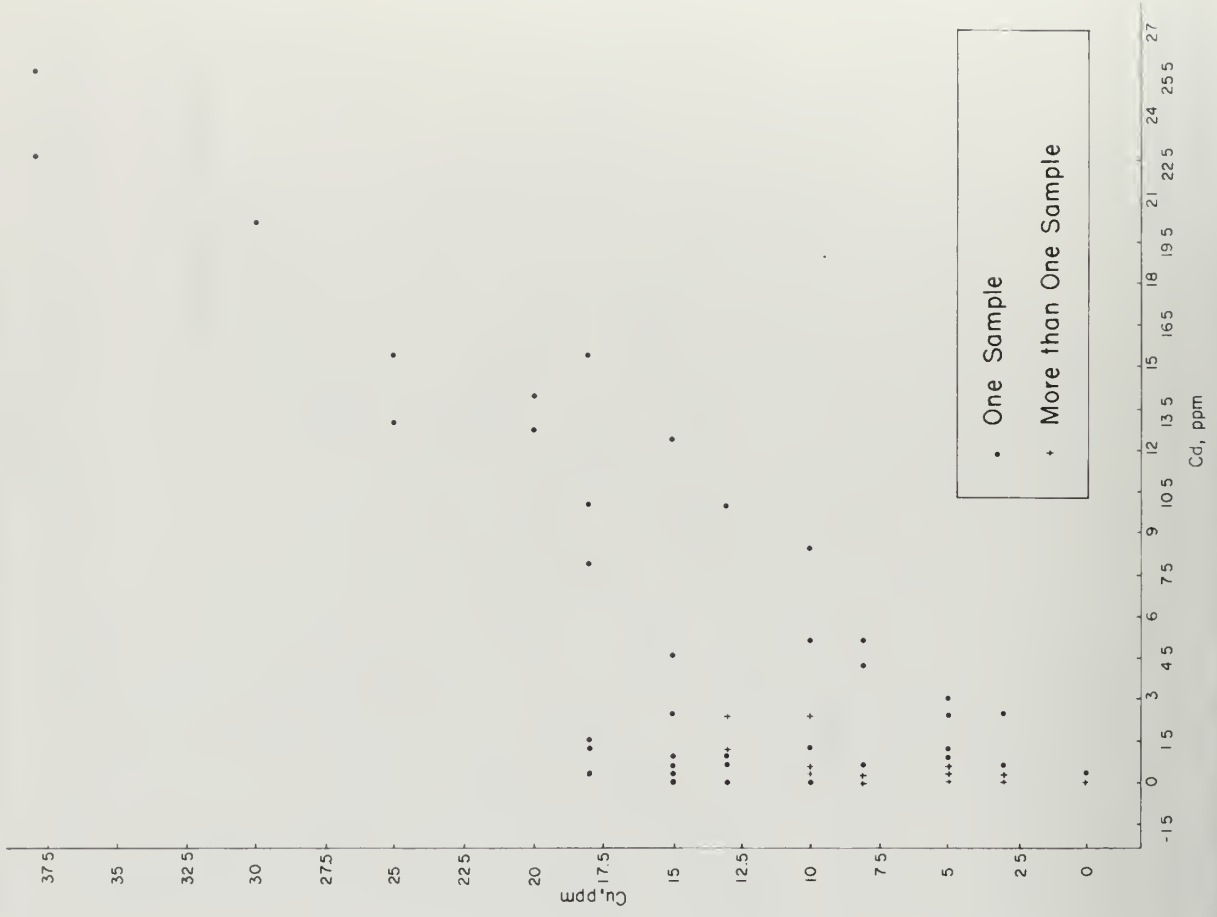


Figure 21. Correlation between cadmium and copper in stream sediments.

Figure 21. Correlation between cadmium and copper in stream sediments.

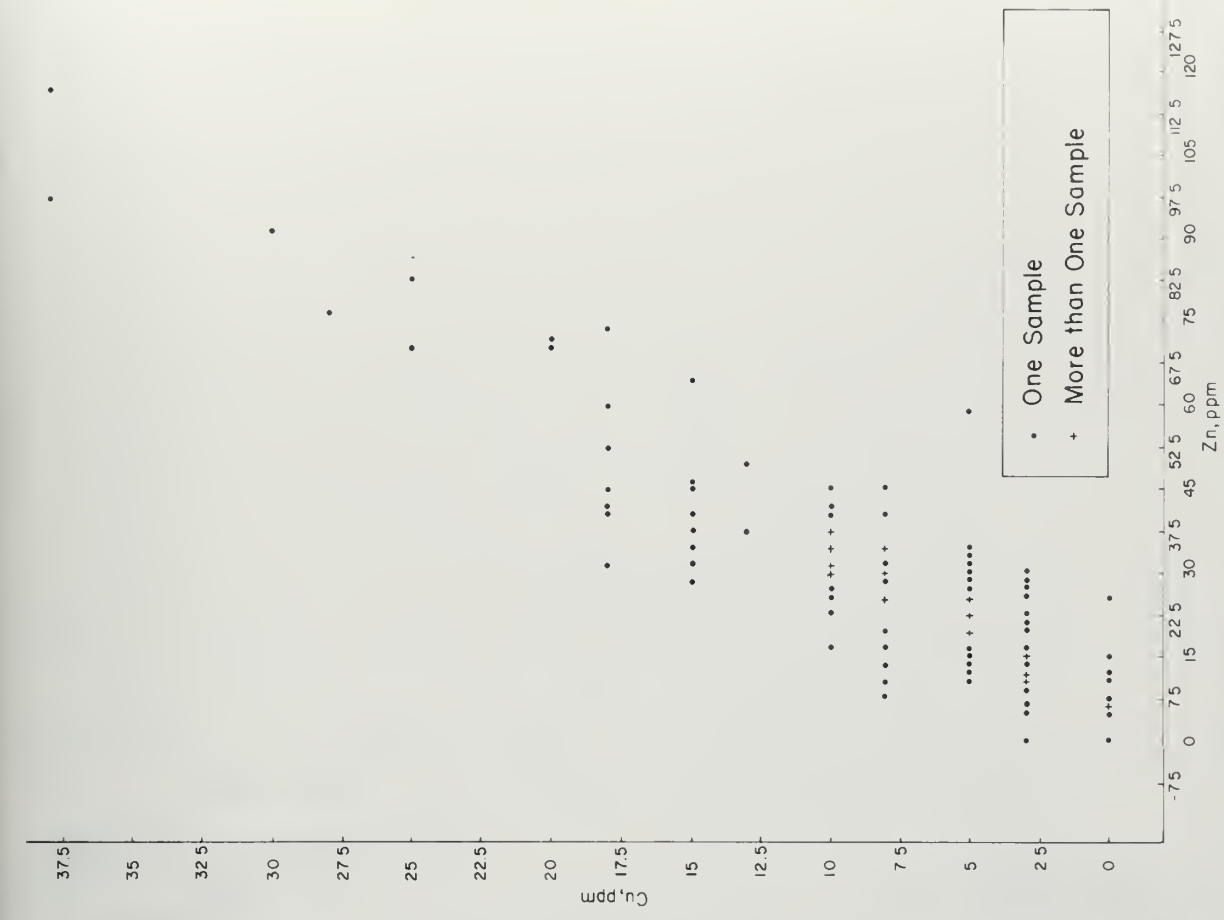


Figure 23. Correlation between copper and zinc in stream sediments.

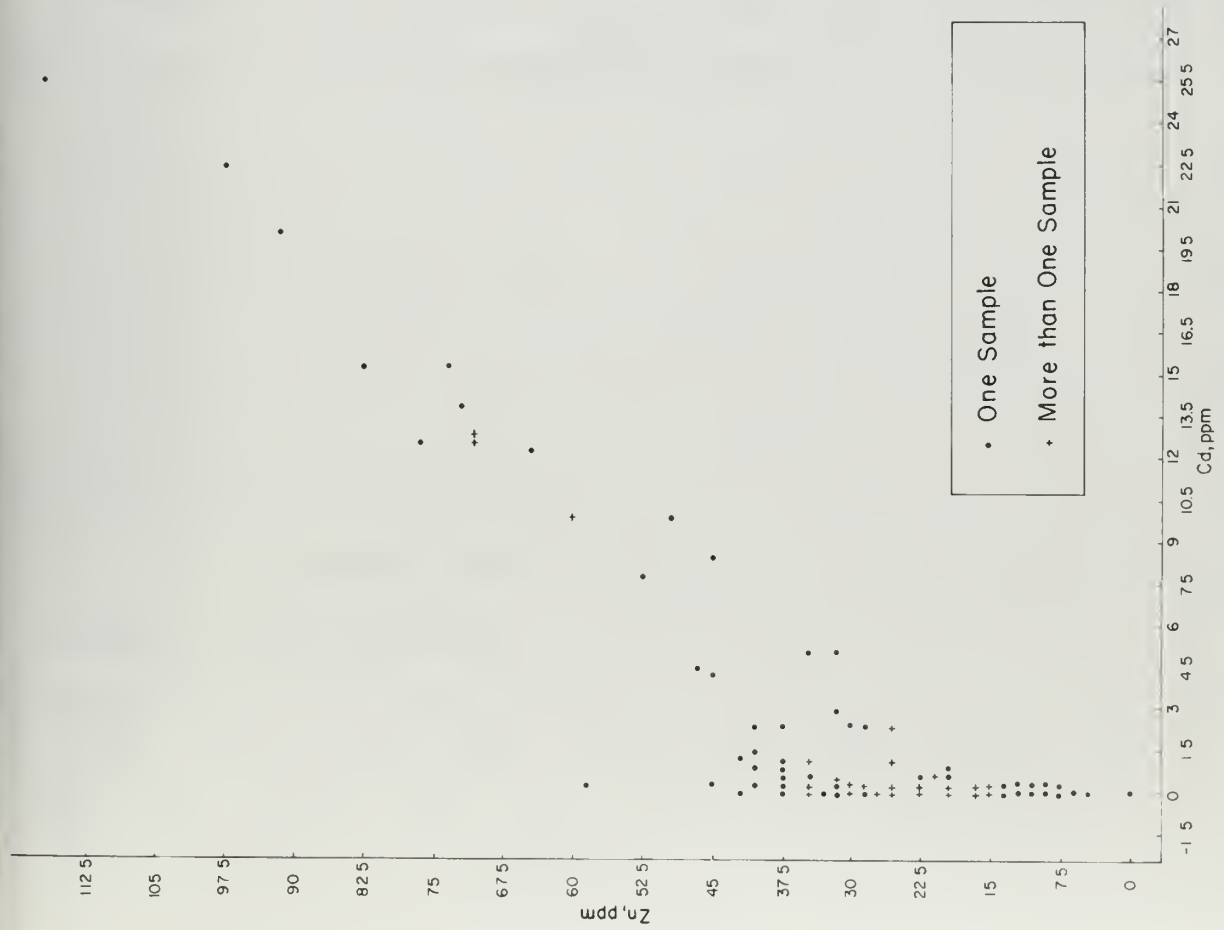


Figure 22. Correlation between cadmium and zinc in stream sediments.

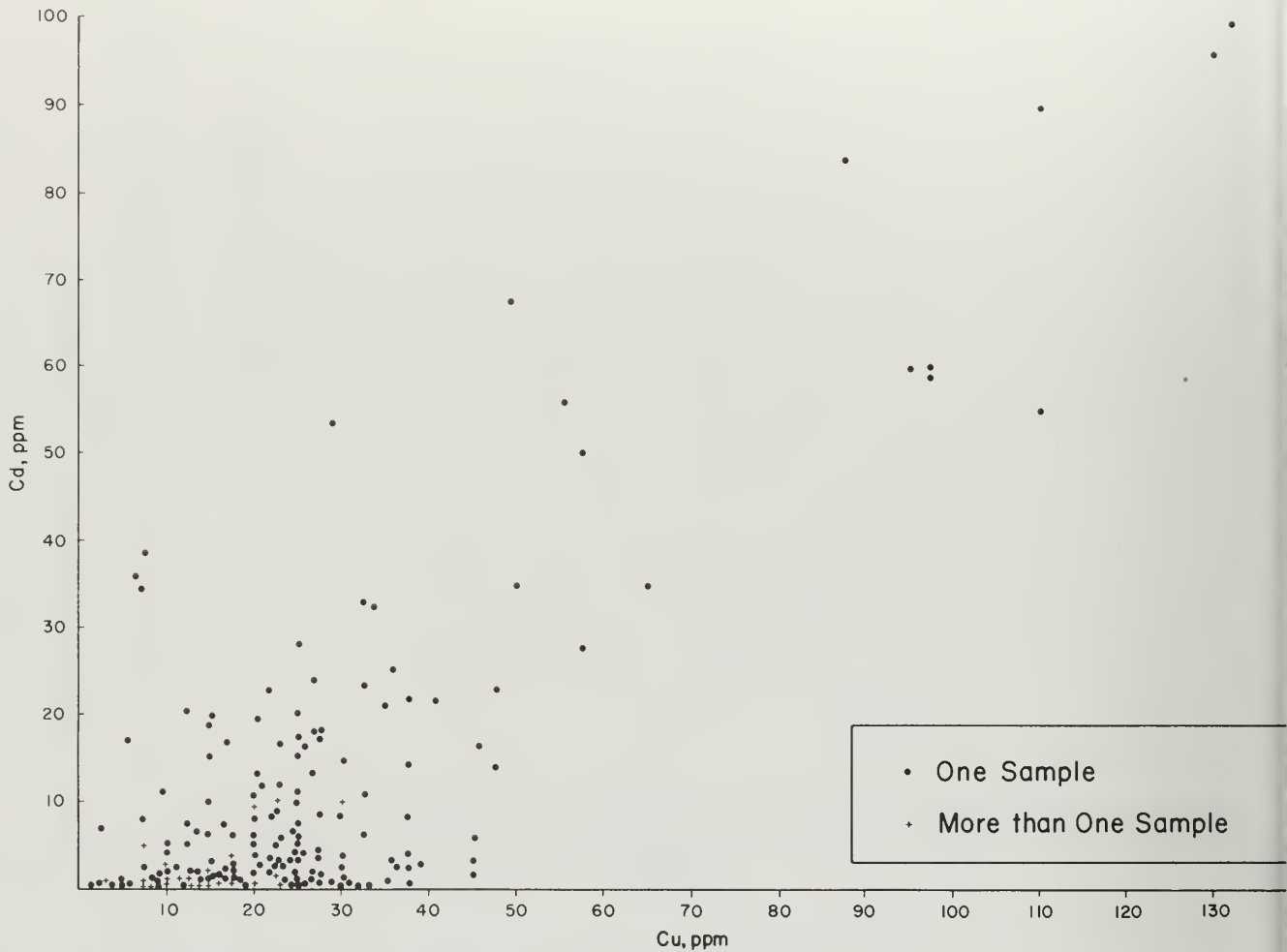


Figure 24. Correlation between cadmium and copper in bedrocks and some stream sediments.

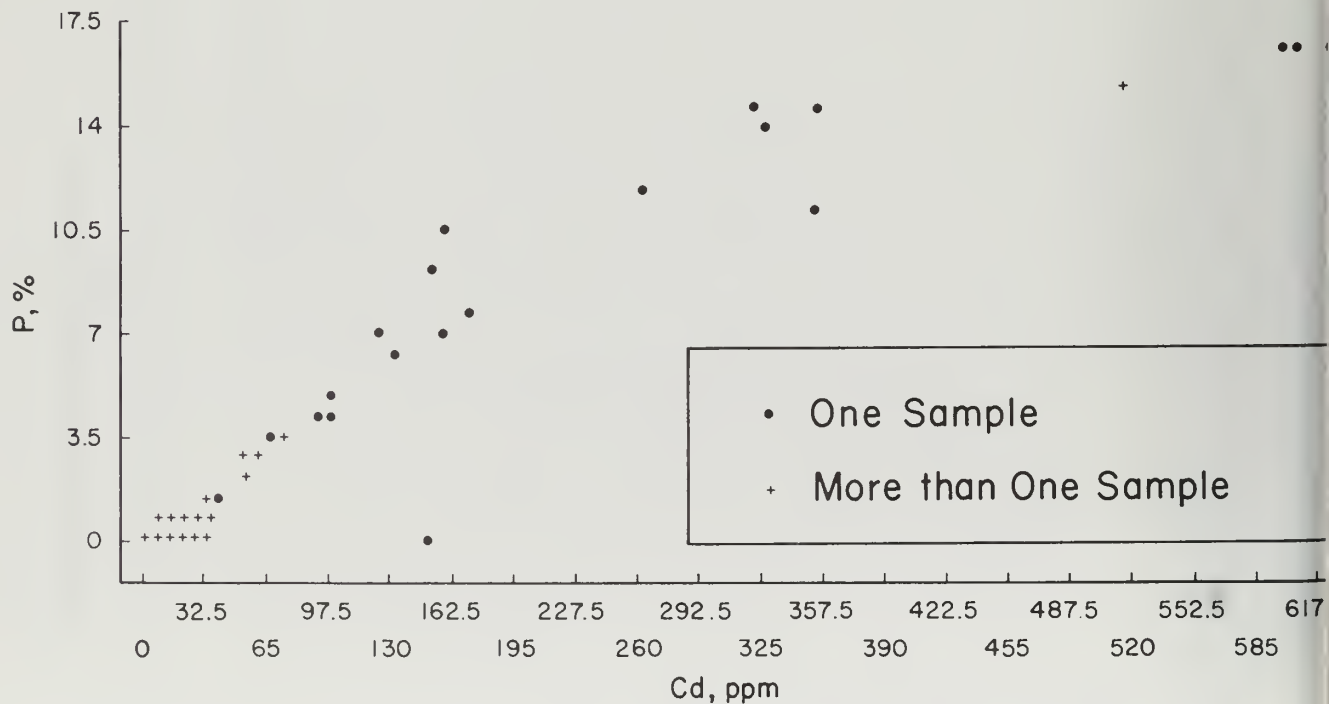


Figure 25. Correlation between cadmium and phosphorus in bedrocks and some stream sediments.

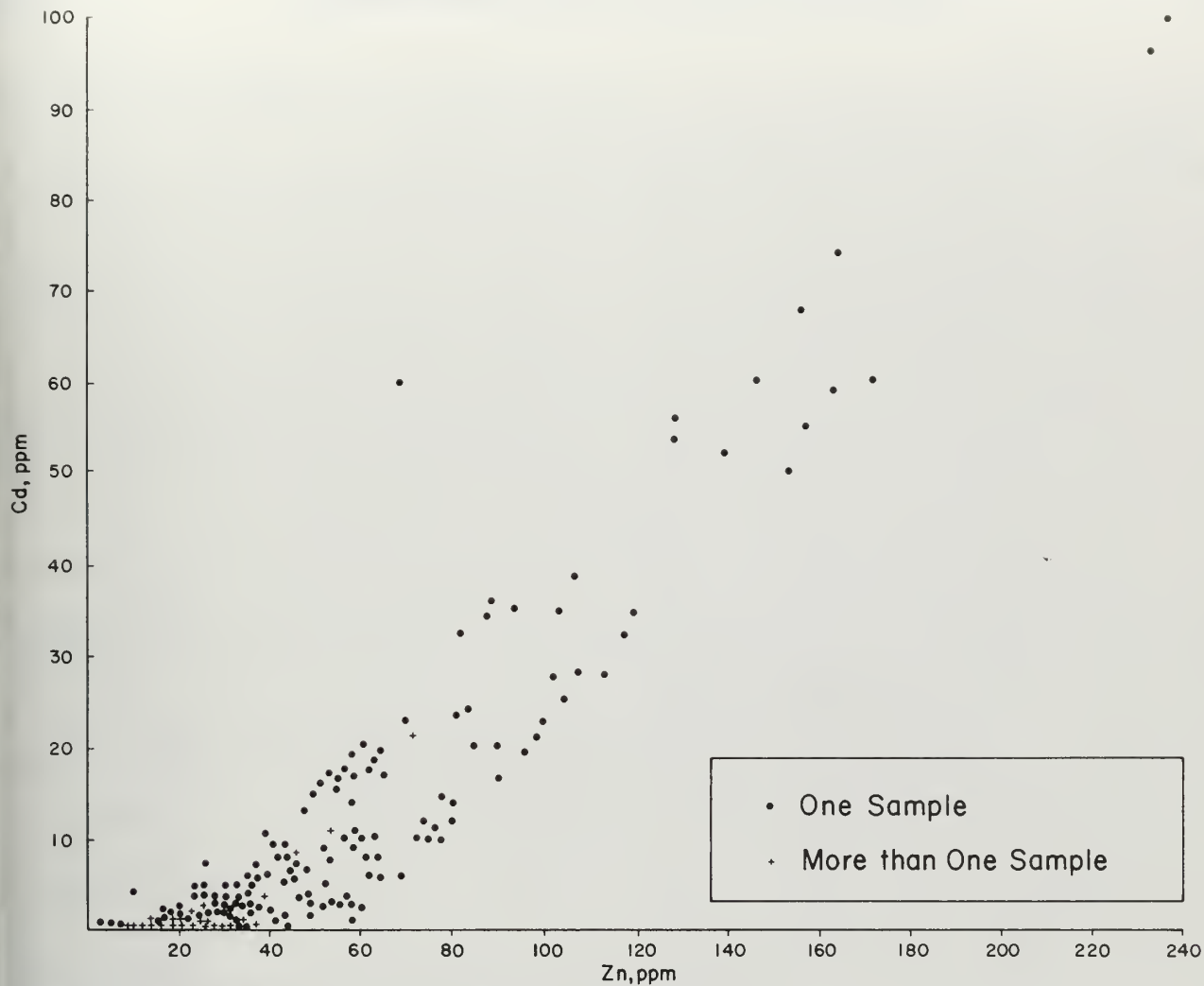


Figure 26. Correlation between cadmium and zinc in bedrocks and some stream sediments.

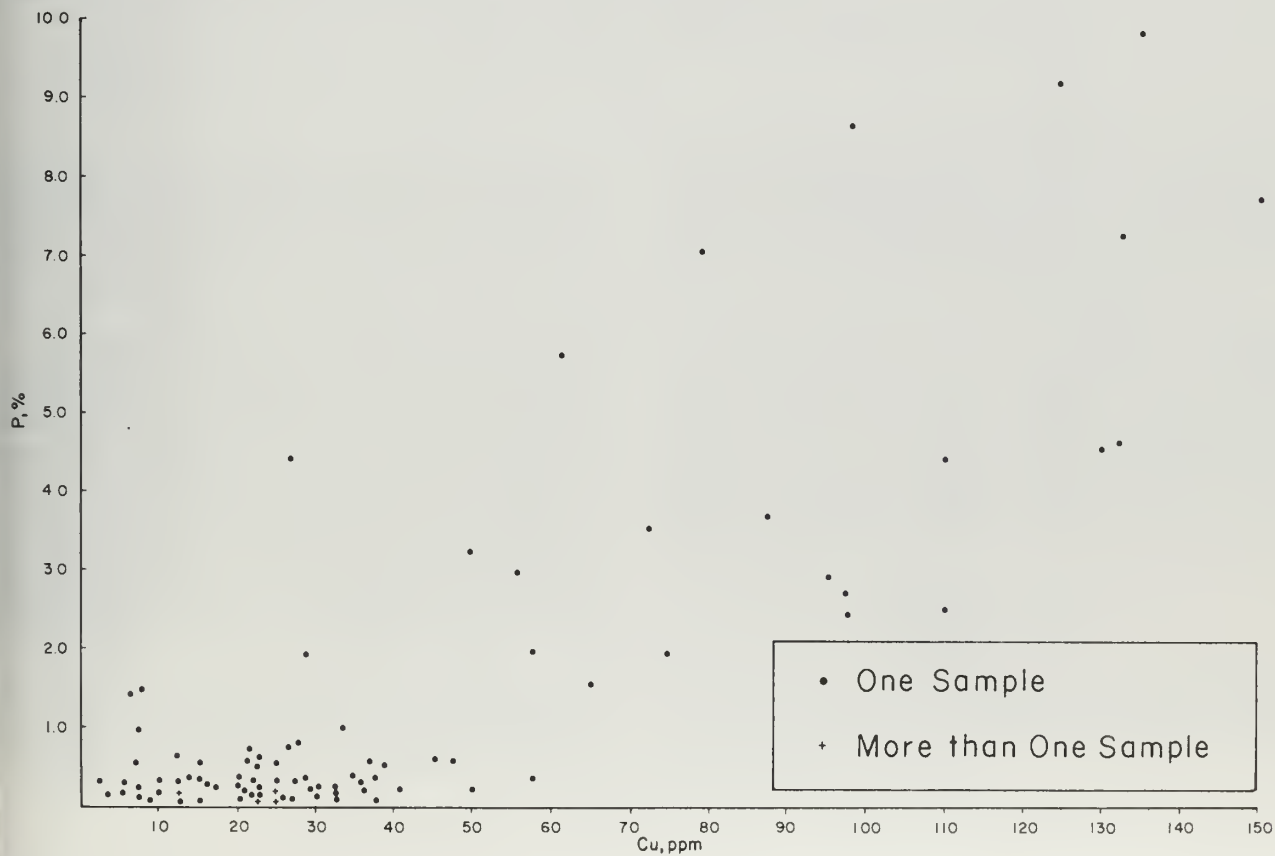


Figure 27. Correlation between phosphorus and copper in bedrocks and stream sediments.

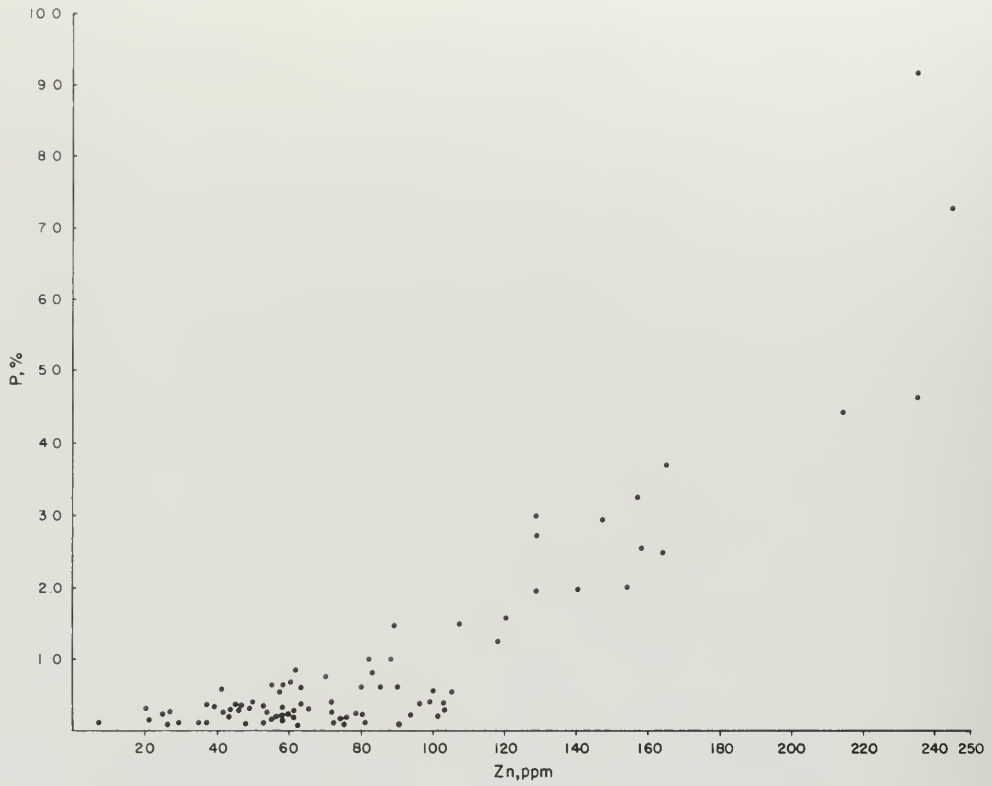


Figure 28. Correlation between copper and zinc in bedrocks and some stream sediments.

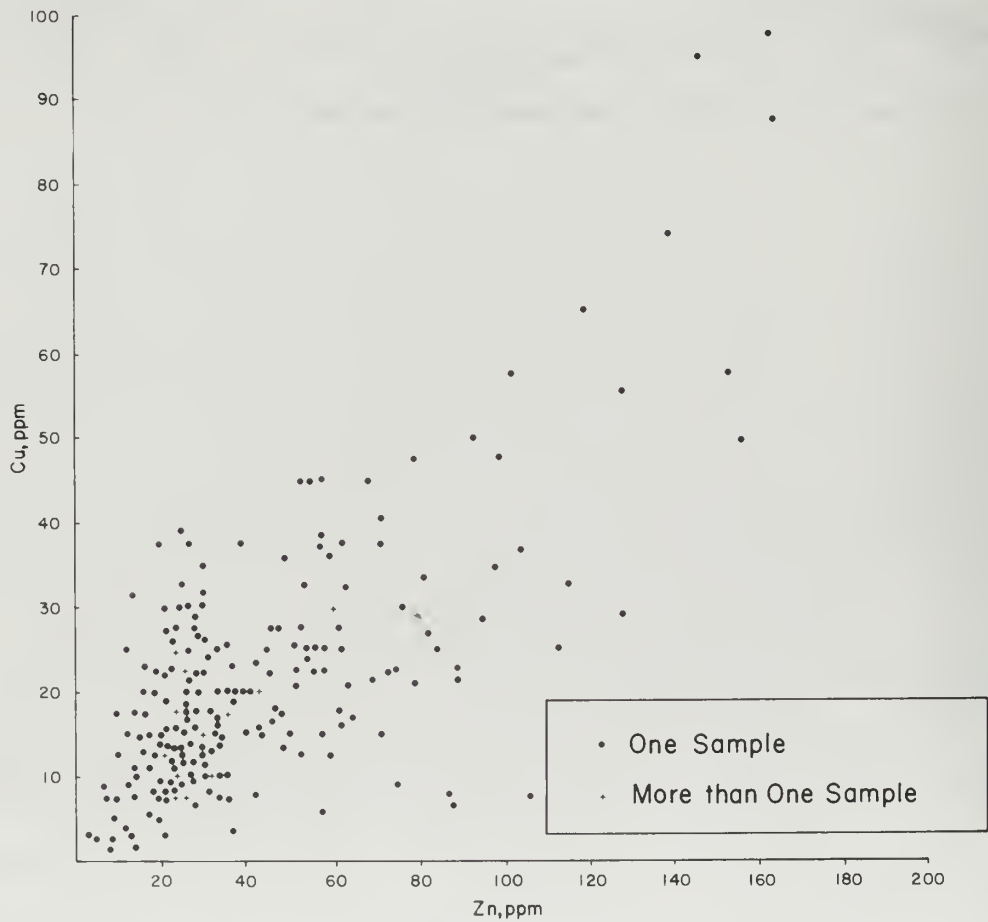


Figure 29. Correlation between phosphorus and zinc in bedrocks and some stream sediments.

Table 5. Correlation of geology¹ and stream sediment chemistry.

Geological Formations	As(ppm)		Cd(ppm)		Cu(ppm)		Pb(ppm)		Hg(ppb)		Zn(ppm)	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Alluvium (8) ² Qa1	0.57-2.86	1.7	0-0.42	0.2	3-8	5	0-20	8	0-40	17	10-35	22
Alluvium/Middle or Lower Pliocene Marine (10) Qa1/Pm1	1.80-4.76	3.4	0.1-0.64	0.4	8-28	14	10-23	16	21-88	44	30-700*	43
Quaternary River Terrace & Fan Deposits (27) Qt	0.10-6.83	1.8	0-13.2	1.6	0-20	7	0-25	10	0-61	24	5-82	26
Quaternary River Terrace & Fan Deposits/ Mesozoic Granitic Rocks (9) Qt/Gr	0.12-1.80	1.0	0-0.6	0	0-10	4	0-13	6	0-46	20	6-34	18
Quaternary Pleistocene Nonmarine (19) Qc	0.70-7.55	2.3	0-0.46	0.1	3-28	10	8-53	18	0-88	16	6-180*	25
Quaternary Plio-Pleistocene Nonmarine (8) Qp	0.65-5.95	2.3	0.04-2.13	0.5	0-5	3	0-28	8	0-53	13	7-25	18
Quaternary Plio-Pleistocene Nonmarine/Middle or Lower Pliocene Marine (10) Qp/Pm1	1.30-6.13	3.2	0.1-1.2	0.8	5-15	11	5-20	9	13-48	30	10-67	35
Upper Miocene Marine (7) Mu	0.50-2.85	1.9	0.14-4.23	1.0	0-15	4	0-25	6	0-48	10	7-50	22
Middle Miocene Marine (24) Mm	0.18-11.40	4.0	0.18-24	7.5	3-23	12	0-20	10	0-512*	25	14-100*	50
Mesozoic Granitic Rocks (21) Gr	0.30-4.25	1.3	0-0.4	0.1	3-13	5	0-15	7	0-41	23	11-57	24
Pre-Cretaceous Metamorphic Rocks (11) m-Ls	0.10-1.93	0.8	0-0.1	0	3-15	6	0-15	5	0-75	24	10-55	27

NOTES:

¹ Refer to Hart, E.W., 1966 for detailed geology of the project area.

² The number in brackets for each geological formation denotes the number of samples taken into consideration for calculating the average values. Also, only units represented by 8 or more samples, were considered in the geology-chemistry correlation.

* Anomalously higher values not considered for average.

the high cadmium contents. High cadmium contents also were found in three samples collected from the crushed rocks in the Rinconada fault zone and in four stream sediment samples from the Hames Valley. According to Burau (Richard G. Burau, University of California at Davis, personal communication, 1954), the soils in Hames Valley also are high in cadmium.

In view of the demonstrated relationships between phosphorus and cadmium, a decision was made to analyse phosphatic samples available from areas outside the study area. In general, phosphatic rocks from other parts of the United States do not necessarily have high cadmium contents (Table 6). Some samples, however, had enough cadmium, (i.e., 110 ppm Cd in phosphate from Idaho) to warrant concern about the possibility of hot pockets of contaminated phosphatic rocks in other United States or world localities. It is therefore recommended, that the U. S. Geological Survey or a similar institution undertake an investigation of cadmium contamination in phosphatic rocks in various locations.

Erhard Bond (personal communication, 1974) of the University of California at Davis has found that samples of phosphatic rock which is exported from Vernal, Utah, to Canada for use as a rock phosphate fertilizer, have a Cd content of 10 ppm.

Some phosphatic rock quarries in Wyoming have 30 to 150 ppm Cd, depending on sample location. Rock from these quarries is used as a rock phosphate fertilizer in the United States and is definitely contaminating agricultural soil and, in turn, the crops which grow on them. These observations support the necessity for further studies of cadmium in phosphatic rocks.

The geology of the study area was correlated with the chemistry of the area (Table 7). Unusually high amounts of cadmium occur in the phosphatic beds of the Monterey and Pancho Rico Formations, in stream sediments of Hames Valley, and in samples from the Rinconada fault zone. These samples are also high in arsenic, copper, lead, and zinc. Perhaps cadmium contamination in the phosphatic rocks is the result of Miocene volcanic activities.

CONCLUSIONS

- Six pairs of elements (As-Cd, As-Cu, As-Zn, Cd-Cu, Cd-Zn, Cu-Zn) in the stream sediments and six pairs of elements (Cd-Cu, Cd-P, Cd-Zn, Cu-Zn, P-Cu, P-Zn) in the bedrock show significant associations.

Table 6. Phosphorus and cadmium determination in samples from other parts of the United States.

Lab. Numbers	P (%)	Cd ppm	Locations	Source
365/73	16.42	11.8	National Bureau of Standard 120a, Florida	National Bureau of Standards, Washington, D.C.
366/73	9.84	30	Pamlico River, North Carolina	Fred Kelley, Cal. Div. Mines & Geol., S.F., CA.
367/73	2.53	1.6	Magdalena Bay, Baja California	Fred Kelley, Cal. Div. Mines & Geol., S.F., CA.
372/73	12.81	11.2	Clay Canyon, Utah	J.H. Madsen, Jr., University of Utah, Salt Lake City, U
373/73	14.21	110	Idaho	L.S. Praler, Bureau of Mines & Geology, Moscow, Idaho
377/73	11.96	60	Pine Mountain, CA	Fred Kelley, Cal. Div. Mines & Geol., S.F., CA.
378/73	8.51	30	Pine Mountain, CA	Fred Kelley, Cal. Div. Mines & Geol., S.F., CA.
379/73	13.35	11.3	San Juan Capistrano, CA	Edmund Kiessling, Cal. Div. Mines & Geol., L.A., CA
380/73	7.94	2.2	Dredge Sample, off so. CA Coast	Jack Veder, U.S.G.S., Menlo Park, CA.
381/73	3.45	13.6	Dos Pueblos Creek, Naples Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
382/73	2.77	21	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
383/73	5.13	50	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
384/73	4.43	31	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
385/73	0.61	4.4	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
386/73	0.20	3.4	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
387/73	0.50	1.6	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
388/73	0.52	3	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
389/73	1.28	2.2	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
390/73	0.21	2	Trench, Chico Martinez Section, CA.	H. Gower, U.S.G.S., Menlo Park, CA.
391/73	15.32	1.6	Florida	D.A. Graetz, University of Florida, Gainesville, Florida
392/73	2.40	3.8	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
393/73	2.80	5	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
394/73	2.90	5	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
395/73	11.50	2	Santa Margarita, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
396/73	4.90	89	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
460/73	1.5	7.5	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
461/73	29.0	22.5	Wheeler Springs, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
462/73	0.11	2.0	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
463/73	3.08	171.5	Santa Margarita, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
464/73	1.46	7.2	Lopez Mountain, CA	Earl Hart, Cal. Div. Mines & Geology, S.F., CA.
466/73	14.05	2.6	Dredge Sample, off So. CA Coast	Jack Veder, U.S.G.S., Menlo Park, CA.
467/73	9.25	1.9	Dredge Sample, off So. CA Coast	Jack Veder, U.S.G.S., Menlo Park, CA.
468/73	9.82	0	Dredge Sample, off So. CA Coast	Jack Veder, U.S.G.S., Menlo Park, CA.
469/73	9.03	1.2	Dredge Sample, off So. CA Coast	Jack Veder, U.S.G.S., Menlo Park, CA.

Table 7. Correlation of geology¹ and bedrock chemistry.

STRATIGRAPHIC CLASSIFICATION OF SAMPLES	MAP SYMBOL	NO. OF SAMPLES	ARSENIC (ppm)		Cadmium (ppm)		COPPER (ppm)		LEAD (ppm)		MERCURY (ppb)		PHOSPHORUS (%)		ZINC (ppm)	
			Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Stream sediments	---	8	4-13	9	3-28	11	10-25	20	10-30	20	0-40	17	0.06-0.16	0.09(4) ²	28-114	66
Rinconada fault zone	---	3	10-14	12	17-22	19	25-38	30	18-27	22	0-43	19	0.17-0.36	0.28	53-72	60
PALEOZOIC Metasedimentary rocks	mSc ^{4/}	2		1		0	19-24	21	12-19	16		0		n.d.	26-31	25
MESOZOIC Granitic rocks	gr,grd, gqd,gb	5	0-2	1		0	12-33	19	15-21	18	0-11	5		n.d.	15-34	24
UPPER CRETACEOUS AND PALEOCENE Unnamed units (marine)	KTg	3	1-3	2		0	9-13	12	16-20	18		0		n.d.	20-25	22
Eocene The Rocks Sandstone	Tr	1		3		0		8		17		15		n.d.		
OLIGOCENE Berry Formation	Tbe	2	0-4	2		0	8-30	19	18-19	19	0-5	3		n.d.	10-26	16
Church Creek Formation	Tce	2		2		0	8-15	12	19-23	21	435-560	498		n.d.	23-33	21
OLIGOCENE-MIOCENE Vaqueros Sandstone (marine)	Tvq Tvt Tvc	3 1 5	1-3 1-3	2 0.5 2		0 0 0	2.5-12.5 10-38 1.5-31.3	6.0 13.8 9.7	15-20 18 16	17 18 16	0-5 2 74	4 2		n.d. n.d. n.d.	9-21 8-14	11 21 17
MIDDLE MIOCENE Monterey Formation	Tmc Tml Tm Phosphatic beds ³	6 15 54 70	1-18 1-17 2-72 3-69	9 6 10 20	0-6 0-6 0-23 3-626	1 2 4 93	18-45 10-38 3-45 7-195	32 21 22 63	18-23 14-30 11-48 15-63	20 22 19 26	0-238 0-78 0-160 0-268	55 8 18 25	0.06-0.10 0.08(9)	3.6	28-64 10-52 3-81 20-468	41 21 31 14
PLIOCENE Santa Margarita Formation	Tsm	1		0		0.2		5	16		0			n.d.		
Pancho Rico Formation (marine)	Tpd Tps Tpi Tpo Phosphatic beds ³ Tus	2 4 4 38 5 11	3-13 2-13 9-17 2-21 1-32 2-14	8 8 14 8 12 6	3-5 0-1 2-5 0-4 7-100 0-7	2 1 3 8-38 29 2	8-10 5-13 8-23 8-38 6-132 3-30	9 9 16 15 41 11	17-25 20-33 24 12-30 18-25 14-24	16 21 24 21 21 19	0-92 0-50 158-300 0-63 8-175 0-48	46 14 216 21 52 11	0.09-0.12 0.11(2)	1.12 0.11(1)	25-32 18-24 21-76 16-64 43-238 9-37	21 21 40 26 85 22
PLEISTOCENE Paso Robles Formation	QTc QTt QTp	1 1 13		4 3 6		1 0 1		20 5 8-38	18 25 19		70 0 11			n.d. n.d. 0.11(1)		31 15 25

¹Durham, 1964a, 1964b, 1966, 1970; Dibblee, 1971, 1972.²Number in parentheses denotes number of samples analyzed for phosphorus.³Phosphatic beds in Monterey and Pancho Rico Formations are not separately mapped.⁴Abbreviations used in Hart, E.W., 1966, Mines and mineral resources of Monterey County.

n.d. = not determined.

Cadmium is present in anomalously high proportions in the King City-San Ardo area, especially in the sediments derived from the Middle Miocene marine Monterey Formation. Cadmium is also unusually high in the phosphatic beds; these beds are the main source of cadmium contamination in the stream sediments and agricultural soils (Lockwood Loam Soil) of the King City-San Ardo area.

Cadmium is the only hazardous element present in quantities that would threaten public health.

RECOMMENDATION

Because similar pockets of cadmium-contaminated phosphate beds may occur elsewhere, such phosphatic materials should be re-evaluated before they are used as raw material for fertilizers.

ACKNOWLEDGMENTS

I thank Glenn A. Borchardt, Edward E. Welday, and Richard M. Stewart for many valuable suggestions and discussions, and for reading the manuscript. Dr. Borchardt assisted me in phosphorus analysis and in computing the data. Duane A. McClure, Thomas H. Rogers, Lydia Lofgren, Charles B. Smith, Earle W. Deneau, and Dorothy L. Hamilton helped with field work, laboratory work, and typing. I also thank Earl W. Hart, Frederic R. Kelley, and Edmund W. Kiessling of the California Division of Mines and Geology; H. Gower, and Jack Veder of the U.S. Geological Survey; J.H. Madsen, Jr. of the University of Utah; L.S. Praler of the Idaho Bureau of Mines and Geology; and D.A. Graetz of the University of Florida, Gainesville, for providing me with the samples mentioned in Table 6.

REFERENCES

- Boyle, T.W., Jr., 1967-1968, Geological map of the San Ardo quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., Jr., 1967-1969, Geological map of the King City quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., 1971, Geological map of the Bradley quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., 1971, Geological map of the Bryson quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., 1971, Geological map of the Junipera Serra quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., 1972, Geological map of the Greenfield quadrangle, California: U.S. Geological Survey open-file map.
- Boyle, T.W., 1972, Geological map of the Saledad quadrangle, California: U.S. Geological Survey open-file map.
- Dham, D.L., 1964a, Geology of the Reliz Canyon, Thampson Canyon, and San Lucas quadrangles, Monterey County, California: U.S. Geological Survey Bulletin 1141-Q.
- Dham, D.L., 1964b, Geology of the Casia Knab and Espinasa Canyon quadrangles, Monterey County, California: U.S. Geological Survey Bulletin 1161-H.
- Dham, D.L., 1966, Geology of the Hames Valley, Winpost and Valletan quadrangles, Monterey County, California: U.S. Geological Survey Bulletin 1221-B.
- Dham, D.L., 1970, Geology of the Sycamore Flat and Paraisa Springs quadrangles, Monterey County, California: U.S. Geological Survey Bulletin 1285.
- Fabi, B.P., 1971, Rapid x-ray fluorescence determination of phosphorus in geologic samples: Applied Spectroscopy, v. 25, no. 1, p. 41-43.
- Flagan, F.J., 1973, 1972 values for international geochemical reference samples: Geochimica et Cosmochimica Acta, v. 37, p. 1189-1200.
- Fletcher, M., and others, 1970, Summary of the literature on inorganic geochemistry of Mercury, in Mercury in the environment: U.S. Geological Survey Professional Paper 713, 67 p.
- Ferguson, L., and others, Cadmium in the environment: Chemical Rubber Company Press, Cleveland, Ohio.
- Furst, A. and Hara, R.T., 1969a, Possible mechanism of metal carcinogenesis, *Offprint from* Physics-chemical mechanism of metal carcinogenesis: The Israel Academy of Sciences and Humanities, Jerusalem, p. 310-320.
- Furst, A., and Hara, R.T., 1969b, A survey of metal carcinogenesis: Progress in Experimental Tumor Research, v. 12, p. 102-133.
- Hart, E.W., 1966, Mines and mineral resources of Monterey County, California: California Division of Mines and Geology County Report 5, 142 p.
- Happs, H.C., 1974, Overview: in Geochemistry and the Environment, v. 1: National Academy of Sciences, Washington, D.C., p. 3-21.
- Harwitz, W., 1970, Official methods of analysis of the Association of Official Analytical Chemists: Association of Official Analytical Chemists, 1015 p.
- Jennings, C.W., 1958, Geologic Map of California, San Luis Obispo Sheet: California Division of Mines and Geology, scale 1:250,000.
- Jennings, C.W., and Strand, R.G., 1958, Geological map of California, Santa Cruz Sheet: California Division of Mines and Geology.
- Lepeltier, C., 1969, A simplified statistical treatment of geochemical data by graphical representation: Economic Geology, v. 64, p. 538-550.
- Riley, J.P., 1958, The rapid analysis of silicate rocks and minerals: Analytica Chimica Acta, v. 19, p. 413-428.
- Sandstead, H.H., and others, 1974, Cadmium, zinc, and lead: in Geochemistry and the Environment, v. 1: National Academy of Sciences, Washington, D.C., p. 43-56.
- Schraeder, H.A., 1970, Expert tells Senate, toxic metal peril rises: San Francisco Chronicle, August 27, 1970, p. 8.
- Schraeder, H.A., and Balassa, J.J., 1963, Cadmium: uptake by vegetables from superphosphate in soil: Science, v. 140, p. 819-820.
- Taylor, S.R., 1964, Abundance of chemical elements in the continental crust, a new table: Geochimica et Cosmochimica Acta, v. 28, p. 1273-1285.
- Vinogradov, A.P., 1959, The geochemistry of rare and dispersed elements in soils: Chapman and Hall, London, 209 p.
- Webber, G.R., 1965, Second report of analytical data for Canadian Association for Applied Spectroscopy syenite and sulfide ore standards: Geochimica et Cosmochimica Acta, v. 29, p. 229-248.

APPENDIX A

Locations of Stream Sediment Samples

Table with columns: LAB. NO., NAME OF MATERIAL, FIELD NO., LOCATION, LONGITUDE DEG. MIN. SEC., LATITUDE DEG. MIN. SEC., NAME OF MATERIAL, FIELD NO., LOCATION, LONGITUDE DEG. MIN. SEC., LATITUDE DEG. MIN. SEC. The table lists 217 stream sediment samples from various locations in California, including Pine Canyon, Arrowood Seco, and San Antonio River.

Location of Bedrock Samples and Some Stream Sediment Samples

Table with columns: LAB. NO., NAME OF MATERIAL, FIELNO., LOCATION, LONGITUDE DEG. MIN., LATITUDE DEG. MIN., FORMATION, LAB. NO., NAME OF MATERIAL, FIELNO., LOCATION, LONGITUDE DEG. MIN., LATITUDE DEG. MIN., FORMATION

Table with columns: LAB. NO., NAME OF MATERIAL, FIELNO., LOCATION, LONGITUDE DEG. MIN., LATITUDE DEG. MIN., FORMATION, LAB. NO., NAME OF MATERIAL, FIELNO., LOCATION, LONGITUDE DEG. MIN., LATITUDE DEG. MIN., FORMATION

APPENDIX B (continued)

Location of Bedrock Samples and Some Stream Sediment Samples

Table with 7 columns: LAB. NO., NAME OF MATERIAL, FIELD NO., LOCATION, LONGITUDE (DEG. MIN.), LATITUDE (DEG. MIN.), FORMATION. The table contains two main sections of data, with the second section starting at the bottom right of the page.

APPENDIX C

Computer Programs

PROGRAM NO. 1.

LIST OF SAMPLE IDENTIFICATION INFORMATION

This program provides a table containing the lab number, name of material, field number, location, county name, latitude, longitude, and formation (or other reference) for each sample.

Card No.	Type
	Job card
	System control cards a) //STEPA EXEC FORTGCLG b) //FORT. SYSIN DD *
	"LIST OF SAMPLE IDENTIFICATION INFORMATION" FORTRAN IV source deck
	System control cards a) //Gφ. FT06F001 DD SYSφUT = A b) //Gφ. FT05F001 DD *
	List of counties (12 cards)

Columns	Format	Entry	Description
1-80	5 (4A4)	A1(K)	Twelve cards each with 5 counties in alphabetical order 5A16 format (Ex: "Alameda," etc.)

			Option card
--	--	--	-------------

Columns	Format	Entry	Description
1-2	12	KFM	Number of personal reference cards to be read (Ex: "26" formations). If "O" none will be read.
3-4	12	LIST	If LIST = O no more list follow, IF LIST ≠ O another list will follow this.

Personal reference cards (optional) If KFM ≠ O, KFM cards are included.

Columns	Format	Entry	Description
1-20	5A4		First 20 columns of KFM cards contain name formation etc., to appear in table.

8. Sample Identification Cards

These are the sample I.D. cards used by the DMG Geochemical Section for each sample submitted for analysis.

Columns	Format	Entry	Description
1-7	A4,A3	X(1), X(2)	Lab number
8-22	3A4,A3	X(3)- (6)	Name of material
23-30	2A4	X(7), X(8)	Field number
31-47	4A4, A1	X(9)- X(13)	Location (nearest geographical feature)
54-55	12	LAT	Degrees of latitude
56-59	F4.2	FLAT	Minutes of latitude to nearest one-hundredth
60-61	12	L	Degrees of longitude with the 100 understood (i.e. "121" degrees is represented by "21").
62-65	F4.2	FLφN	Minutes of longitude to nearest one-hundredth
69-70	12	ICO	County number (see alphabetical list of 58 counties) 59 = "OUT OF STATE" = blank
79-80	12	IFM	Personal reference number (Ex: number of formation from list of formations to be read in)

9. End Card

9's in all columns

10. Repeat cards 6 - 9 if LIST ≠ O

11. System control card

/*

STORAGE AND RETRIEVAL OF CHEMICAL ANALYSES*

The format for entering chemical data on computer cards is the periodic table. Data for the first ten elements can be entered on the first card. The format for entering these ten elements is: (10 (A1, F6.2), 2A4, 1X, 11). Hydrogen (atomic no. 1) would be entered in columns 2 to 7. Helium ($Z=2$) would be entered in columns 9 to 14. Oxygen would be entered in columns 51–56. These are the 6 columns prior to and including column 56 (atomic no. 8 times 7 columns per element). Columns 1, 8, and 50 can be used to indicate whether the data is in ppm (), ppb (*), or percent (%). Since oxygen is included as one of the elements, all other data is reported in the elemental form. Lab numbers are right adjusted in columns 72–78.

Cards for the remaining elements in the periodic table are prepared in the same way. Column 80 is used to indicate the decade of the atomic number. For example, data for cadmium ($Z = 48$), would be in columns 51–56 of a card with the number 4 in column 80. Data for tin ($Z = 50$) would be in row 10 of the same card since $Z = 50 (4 \times 10 + 10)$.

Only numbers and decimal points can be used in the data columns. The only exceptions are columns 1, 8, 15, 22, 29, 36, 43, 50, 57, and 64 used to indicate data in other than ppm concentrations.

The advantages of this method of data entry are:

1. Subsequent analyses of additional elements can be added to the data set without repunching the old data.
2. The systematic order of the elements remains unchanged with the addition of new analyses.
3. New users of the system could probably locate data for the elements simply by knowing that it was "based upon the periodic table."

A disadvantage of the system is the large number of cards needed to represent an analysis. All ten cards representing the periodic table need not be included unless the analysis happens to have elements from each decade of the periodic table.

*This format is only used to punch the computer cards.

PROGRAM NO. 2.

TABLE OF CHEMICAL ANALYSES

This program provides a table containing chemical analyses. The cards for the input are prepared as explained above in "Storage and retrieval of chemical analyses."

Card No.	Type
1.	Job card
2.	System control cards 1) //STEPA EXEC FORTGCLG b) //FORT. SYSIN DD*
3.	"TABLE OF CHEMICAL ANALYSES" FORTRAN IV source deck

4. System control cards
a) //STEPA EXEC FORTGCLG
b) //FORT. SYSIN DD*

5. Data card A (column 80 = 1)

Column	Format	Entry	Description
30–35	F6.2	Phosphorus (%)	

6. Data card B (column 80 = 2)

58–63	F6.2	CU	Copper (ppm)
65–70	F6.2	Zn	Zinc (ppm)

7. Data card E (column 80 = 3)

16–21	F6.2	As	Arsenic (ppm)
-------	------	----	---------------

8. Data card D 1 (column 80 = 4)

51–56	F6.2	CD	Cadmium (ppm)
-------	------	----	---------------

9. Data card E (column 80 = 7)

65–70	F6.2	HG	Mercury (ppb)
-------	------	----	---------------

10. Data card F (column 80 = 8)

9–14	F6.2	PB	Lead (ppm)
72–78	2A4	AN ϕ , Z	Lab number

Repeat cards 5 through 10 for each sample.

11. End card

9's in all columns

Repeat card 11 five more times. (The number of end cards is equal to the number of data cards representing a sample, 6 in this case.)

12. System control card

/*

This program can be adapted to other elements as the need arises.

PROGRAM NO. 3.

STEPWISE REGRESSION ANALYSES

This program computes a multiple linear regression equation in a stepwise manner, giving correlation matrix and plotting correlation curves for various elements. This program was written by the Health Sciences Computing Facility of University of California, Los Angeles; refer to its program # BMDP2R details.

APPENDIX D

Digestion Procedures

TOTAL DIGESTION TECHNIQUE
(CLOSED DIGESTION SYSTEM)

Ordinary digestion techniques could not be employed on samples to be tested for mercury and other volatile elements, because of the danger of losing them due to their volatility. Therefore, reflux heating of the digest in a closed system was required during sample preparation. Wet digestion of the samples was achieved with a 1:1 mixture of concentrated nitric and sulfuric acids, with the apparatus (Figure 30) in a reflux position.

Apparatus

The apparatus mainly used for digesting samples for mercury analysis consisted of a digestion flask, a modified soxhlet extractor, a dropping funnel, and a Friedrichs condenser.

The digestion apparatus (Figure 30) is a modified version of that used by the Association of Official Analytical Chemists (Horwitz, 1970) to digest fruit pulps and other vegetables for mercury determinations. All units of apparatus are made from Pyrex glass. Unit 3 is a modified soxhlet extractor, 5 centimeters in outside diameter, with a 250 millimeter capacity, a facility to overflow, and without an inner siphon tube but equipped with a stopcock on the tube leading to the digestion flask, unit 1. With the stopcock open, the apparatus is in the reflux position, when closed, this unit serves as the trap for condensed steam and acid fumes. The top of the unit is attached to a 34-cm-long Friedrichs condenser, unit 4. The bottom of unit 3 is attached through the center neck of a two-neck, round bottom, 500 ml digestion flask, unit 1. The two necks of this flask are 3 cm apart to provide working clearance. The offset neck is used to attach a 10-ml dropping funnel, unit 2.

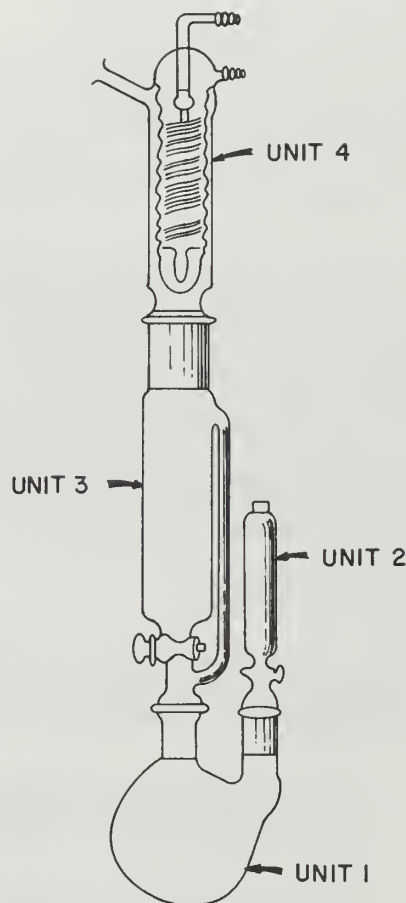
Because mercury compounds tend to absorb the glassware surfaces, this apparatus and the separators were rinsed with a dilute HNO_3 , and then with deionized distilled water. Also, during the course of digestion of a series of samples, blanks were run and checked for possible contamination at least twice a week. The usual workload was eight samples a day.

Reagents

- 1. Concentrated HNO_3 (Baker Special, suitable for mercury determination);
- 2. $\text{HNO}_3 - \text{H}_2\text{SO}_4$ mixture (1:1); and
- 3. Urea - 40 percent (W/V)

Procedure

Thoroughly mix the pulverized sample on a plastic sheet and spread it flat. Weigh 10 gm of the sample by taking increments from all sides, corners and grids in order to get a representative sample from the pulverized bulk powder. Drop this powder in the digestion flask and dampen it with a few ml of (1:20) HNO_3 . Let it stand overnight; or



- UNIT 1. DIGESTION FLASK
- UNIT 2. DROPPING FUNNEL
- UNIT 3. MODIFIED SOXHLET EXTRACTOR
- UNIT 4. FRIEDRICH CONDENSER

Figure 30. Digestion apparatus for volatile elements.

2. Heat gently on a heating mantle by setting rheostat at 30 volts for 20 to 30 minutes. The stopcock should be kept in a reflux position while heating.
3. Add, dropwise, 30 ml $\text{HNO}_3 - \text{H}_2\text{SO}_4$ (1:1) mixture. Change the rheostat to 60 volts. Heat until dense white H_2SO_4 fumes cease with stopcock in the reflux position.

Note: Because nitrous oxide fumes rise into the reflux condenser, it is necessary to rinse the apparatus from the top with a minimum amount of deionized distilled water. While rinsing, care should always be taken not to increase the volume significantly.

4. Boil for one hour. Count the time after the first bubble starts.

5. After boiling for one hour, add 10 ml concentrated HNO₃. Heat for 15 minutes more.
6. Rinse the apparatus with water.
7. Add 10 ml of 40 percent urea. Close the stopcock. Heat and collect the solution in the soxhlet extractor, Figure 30, unit 3, for 15 to 20 minutes.
8. Shut down, cool and pour all the contents of the flask, including the fine suspended particles, into a 250-ml volumetric flask. Cool, make to volume with distilled water and transfer to a polyethylene bottle.
9. Prepare blank solutions in the same way and check for possible contamination.

Important Note: Do Not Filter. When taking an aliquot for mercury determination, agitate the bottle and include the suspended particles in the aliquot. If filtered, the mercury determined is always less than the amount present in the sample. For the determination of other elements, filter and then take the aliquot. For arsenic determination, it is necessary to use a special treatment to remove the nitric acid present in the digest because it hinders the arsenic determination. Nitric acid was completely removed from sample digests by slowly heating with concentrated sulfuric acid until brown fumes of nitrous oxide were no longer visible and white, dense fumes of sulfuric acid evolved.

TOTAL DIGESTION TECHNIQUE (OPEN DIGESTION SYSTEM)

Because of the contamination problem, discussed earlier in the test, various digestion techniques were developed and tested to digest the bedrock samples. The following is the account of these techniques:

- Method A** – Mechanically agitate 10 gm of sample for one hour with 20 ml of 2N HNO₃. After agitation, decant the solution for analysis.
- Method B** – Heat 5 gm of sample for two hours with 40 ml of 2N HNO₃; cool and dilute to 100 ml volume with deionized water.
- Method C** – This is the total digestion technique used in digestion of stream sediments. Heat 10 gm of sample in a special closed digestion apparatus with a mixture of 40 ml HNO₃ and H₂SO₄ (1:1) and 10 ml of 40 percent urea; cool and dilute to 250 ml volume with deionized water.

Method D – This may be called an open version of the total digestion technique described in C. Heat 10 gm of sample with a mixture of 40 ml HNO₃ and H₂SO₄ (1:1) and 10 ml of 40 percent urea in sand bath on a hot plate.

Method E – This technique is used mainly in rapid sili-
analysis and is known as the B solution method (Riley, 1958). Heat 0.5 gm of sample in test crucibles on water bath, with 10 ml perchloric and 15 ml hydrofluoric acids; cool and dilute the crucibles to 500 ml with deionized water.

Table 8 shows the results of analyses of 15 samples digested by using all the above techniques. It is clear that methods B and C bring out most of the cadmium in solution. Method E requires a long digestion time and is not desirable for samples having low cadmium contents as there is a dilution factor of 1000 involved. Therefore, the remaining samples were digested by method D for cadmium determination.

An attempt was made to use hydrochloric acid instead of nitric acid in methods A and B. However, this produced very white precipitates which interfered with the analysis by atomic absorption spectrophotometer, so nitric acid was used throughout.

Past experience with marine and stream sediments showed the necessity of using the closed digestion technique for mercury and other volatile elements. As the phosphatic samples seemed to raise a special problem, it was decided to compare the results of digests obtained by methods C (closed digestion) and D (open digestion) for arsenic, copper, lead, mercury, and zinc. No appreciable differences were found in the resulting analyses.

All the samples were digested by method D for all analyses except cadmium. This was contrary to prior experience and probably can be explained by the lack of methyl mercury in the bedrock samples, thus allowing the use of an open digestion system.

ACID EXTRACTION TECHNIQUE

The detection limit in samples digested by the total digestion technique was too low to measure cadmium in the low concentrations in which it occurs in some of the stream sediment samples. Therefore, an acid extraction method was utilized in which 20 g of the pulverized sample in a bottle with 40 ml of (two molar) HCl was shaken for one hour on a mechanical shaker. After one hour, the suspension was filtered and used for cadmium determination.

Table 8. Comparison of various digestion techniques.

SAMPLE #	METHOD A	METHOD B	METHOD C	METHOD D	METHOD E	Values considered for report are calculations.
101/73	36.5 ⁽²⁾	89.5 ⁽²⁾	28.0	59.5	90.0	90.0
111/73	19.5 ⁽²⁾	22.6	15.0	18.8	20.0	22.6
112/73	15.0 ⁽²⁾	19.4	14.0	16.3	20.0	20.0
115/73	75.5 ⁽²⁾	96.0	64.6 ⁽²⁾	66.3	70.0	96.0
116/73	41.5 ⁽²⁾	47.2	39.0	41.0	50.0	50.0
121/73	19.8 ⁽³⁾	38.5 ⁽²⁾	16.0	17.5	30.0	38.5
155/73	32.0 ⁽²⁾	32.8	20.0	27.3	30.0	32.8
159/73	72.5 ⁽²⁾	166.0	21.0	43.8	150.0	166.0
160/73	57.5 ⁽²⁾	121.0 ⁽²⁾	22.0	35.5	120.0	121.0
162/73	22.0 ⁽²⁾	27.6	24.5 ⁽³⁾	23.0	27.0	27.6
167/73	225.0 ⁽²⁾	348.0	68.0	92.5	300.0	348.0
168/73	175.0 ⁽²⁾	348.0	53.0	75.0	330.0	348.0
171/73	46.5 ⁽²⁾	52.0	42.7 ⁽²⁾	32.3	50.0	52.0
206/73	29.5 ⁽²⁾	32.2	23.2	26.3	20.0	32.2
277/73	43.4 ⁽²⁾	99.0	25	48.5	100.0	100.0

Note: The figure in parentheses is the number of times the sample was digested, and the value given is the average of this number.

APPENDIX E

Analytical Techniques

MERCURY

Apparatus

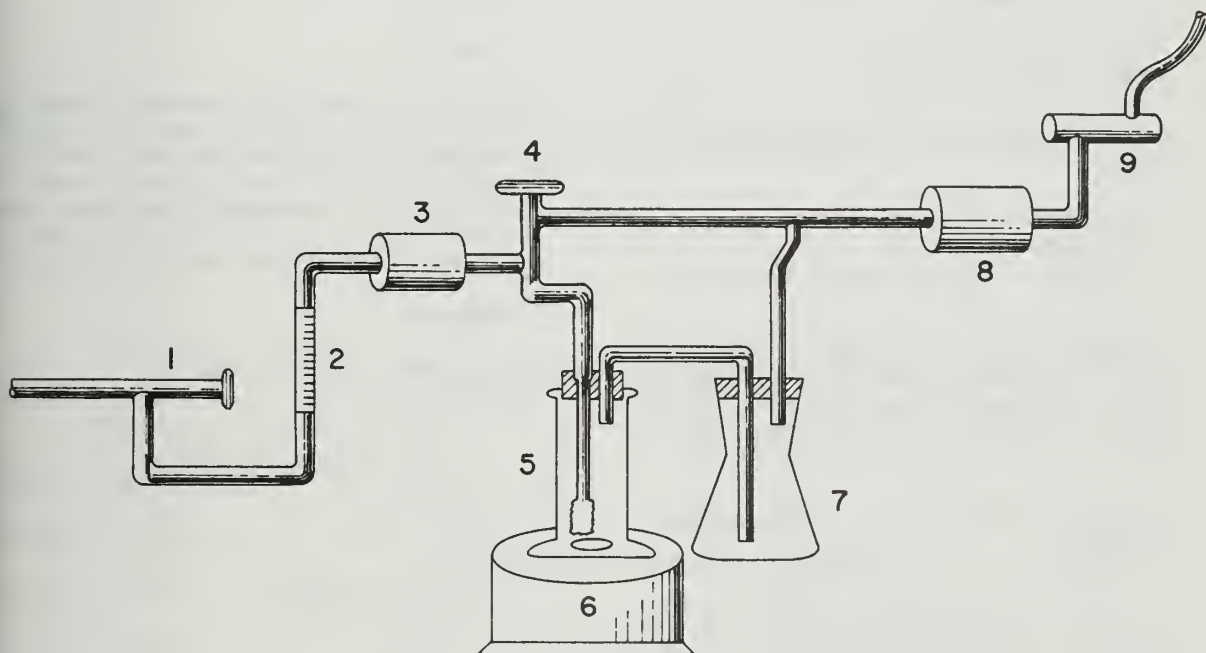
1. Atomic Absorption Spectrophotometer: Perkin Elmer, Model 403, equipped with concentration read out, deuterium background corrector, mercury hollow cathode lamp and a chart recorder, model 165.
2. Laboratory kit for flameless mercury determination: Refer to Figure 31. This device was assembled in the Division laboratory as follows:
 - a) Needle valve: Lab-Crest threaded, glass needle valve, with angle design;
 - b) Flowmeter: Monostat air-flowmeter;
 - c) Reaction vessel: prepared by cutting a 1000 ml plain hydrometer pyrex cylinder in half;

- d) Absorption cell: made up of clear, transparent, plastic tube, 2.5 cm o.d. and 10 cm length, with quartz end windows.

Additionally there are moisture traps, a dehydration trap, and a trap to remove mercury from the incoming air, if any is present. The whole system is an open system.

Reagents

1. Stannous Chloride solution: 10 percent weight/volume prepared in 20 percent HCL. Prepared fresh every 2 to 3 months.
2. Anhydrous (magnesium perchlorate): commercially available.
3. Mercury standards: stock solution of 1000 ppm Hg, purchased from Harleco, was used to prepare the working standards. Serially dilute to 0.1, 0.5, 1, 5, 10,



1. NEEDLE VALVE
2. AIR-FLOWMETER
3. ACTIVATED CHARCOAL TRAP
4. TWO-WAY STOPCOCK
5. REACTION VESSEL

6. MAGNETIC STIRRER
7. MOISTURE TRAP
8. DEHYDRATION COLUMN
9. ABSORPTION CELL WITH QUARTZ WINDOWS

Figure 31. Non-flame mercury device.

and 25 ppb Hg, using 10 percent HCl. Because of the acid diluting medium for the standards, the mercury values remained reasonably uniform and were used for a period of one week before fresh working standards had to be prepared. The standard blank was prepared in the same way, and each blank was tested for any possible contamination. One of the standards was run as an unknown between each batch of samples to check reproducibility.

4. Activated charcoal and glass wool.

Procedure for Flameless Mercury Measurement

1. Set up the atomic absorption (AA) unit with the Hg hollow cathode lamp and with flow-through absorption cell in place of burner, keeping the following settings:

Wavelength - 253.7 Å

Slit setting - 5 (3 mm, 20 Å)

Lamp current - 10 milliamps (mA)

Air flow rate - 835 ml/min at 1 atmosphere and 70° F. This can be adjusted by keeping the stainless steel ball in the air-flowmeter at 8.

Concentration mode - 1-80 (approx.)

Adjust wavelength for maximum energy; align absorption cell for minimum absorbance.

2. Turn on the deuterium background corrector and let it warm for 10 to 15 minutes.
3. Turn on the chart recorder keeping the following settings:

Input switches - float and negative

Chart speed - 5 mm/min

Power Knob - "Amp" for warm-up and then to "Servo."

4. Keep the clean reaction vessel with a two-way stopcock in the by-pass position. Keep the magnetic stirrer in an off position, and adjust the air flow at the rate of 835 ml/min. Zero the instrument with the blank mercury-free air.
5. Change the activated charcoal, anhydrous and glass wool daily.
6. Take 100 ml deionized H₂O in a reaction vessel and pipet 10 ml of the standard or agitated and unfiltered sample solution. If standards are used, start with the lowest concentration. The standards which were used for the present analysis contained 1, 5, 10, and 25 ppb Hg, respectively.
7. Turn the knob of the chart-recorder from "Servo" to "Chart." Before starting the actual analysis, adjust 0 and 100 percent concentration using the ZERO and GAIN controls of the recorder. Use blank (100 ml H₂O + 2 ml 10 percent SnCl₂) for adjusting 0 percent and 25 ppb Hg standard for adjusting 100 percent.

8. Add 2 ml of 10 percent SnCl₂, using a 2 ml tip-up pipette. Close the reaction vessel immediately.

9. Start the magnetic stirrer and activate aeration by turning on the two-way stopcock. Numerical readout of the instrument and the readout on the recorder will be recorded simultaneously. Write the identifying sample or standard number on chart paper.

10. When the intensity in ppb reaches zero on the readout of the instrument, turn off the magnetic stirrer switch aeration to bypass position, and remove the stopper from the reaction flask. At the same time change recorder from "Chart" to "Servo."

11. Rinse down the fritted aeration tube with HNO₃ (1:20) and then with distilled water. About once a week, or more often if necessary, this fritted aeration tube is cleaned in an ultrasonic bath, because the digest contains suspended particles that fill the pores in the fritted portion of the aeration tube.

Figure 32 represents the working curve drawn from the peak obtained on AA recorder by running various standards. This curve was used for all samples to convert observed peak height into corresponding concentrations.

(b) ARSENIC

Apparatus

All arsenic determinations were carried out on a Perkin Elmer 403 atomic absorption spectrophotometer equipped with a three-slot burner head, model 165 chart recorder, and a deuterium background corrector. The device used for arsine generation (Figure 33) is a laboratory assembled device consisting of a reaction flask, dosing column, collection balloon, and a four-way stopcock.

Reagents

1. Concentrated hydrochloric acid.
2. Potassium iodide solution (15 percent)
3. Stannous chloride solution - 20 percent in 8N HCl
4. Zinc - granular, 20 mesh, analytical reagent grade
5. Arsenic standard - stock solution of 1000 ppm As was prepared as follows:
 - a) Weigh exactly 1.320 gm As₂O₃ (A.R. grade) and dissolve in 25 ml of 20 percent potassium iodide.
 - b) When the powder is dissolved completely, neutralize this solution to a phenolphthalein endpoint with 20 percent H₂SO₄.
 - c) Dilute to one liter with 1 percent H₂SO₄.

From this stock solution, working standards of 5, 10, 25, 35, and 50 ppb As were prepared fresh daily.

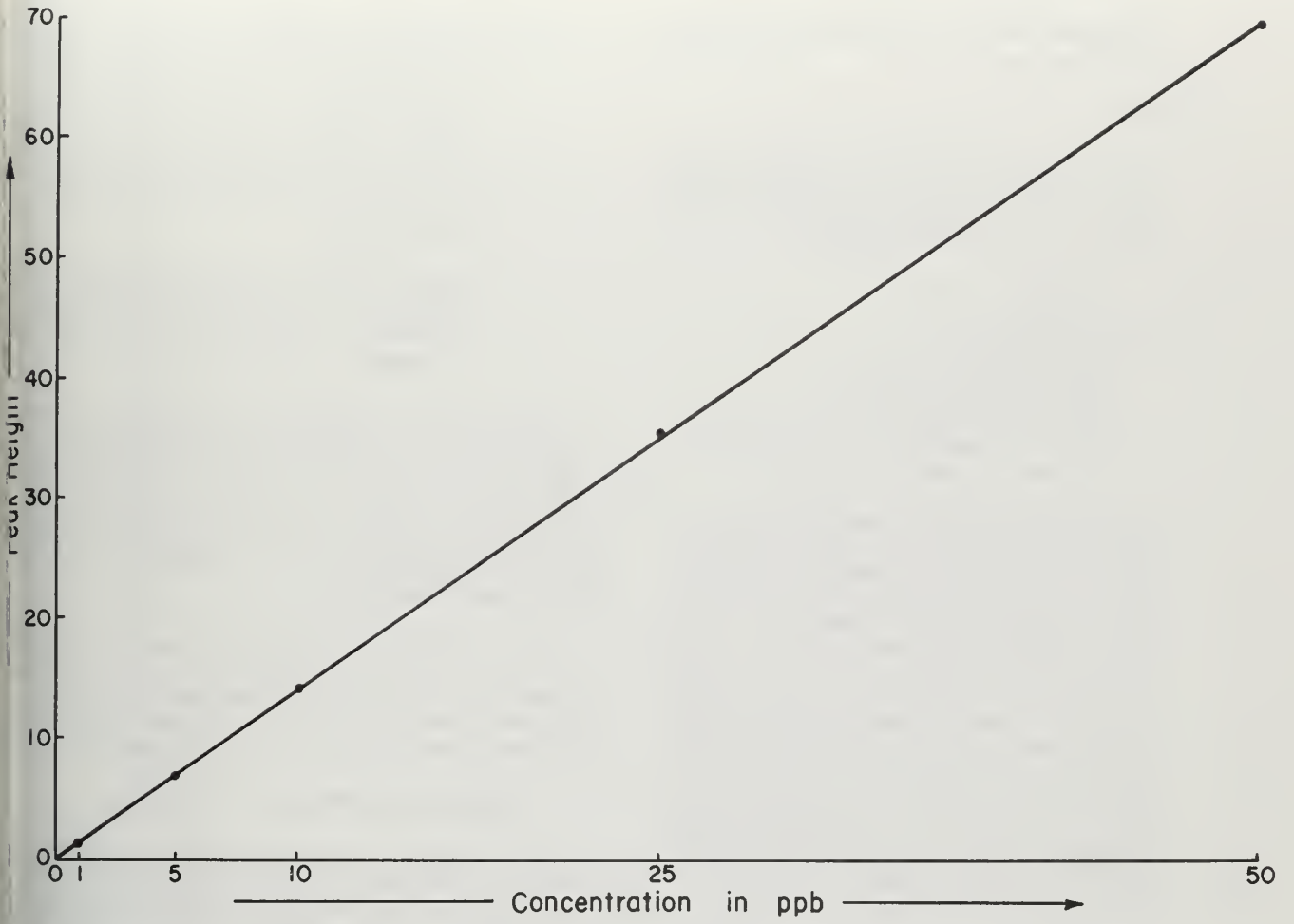


Figure 32. Working curve for mercury.

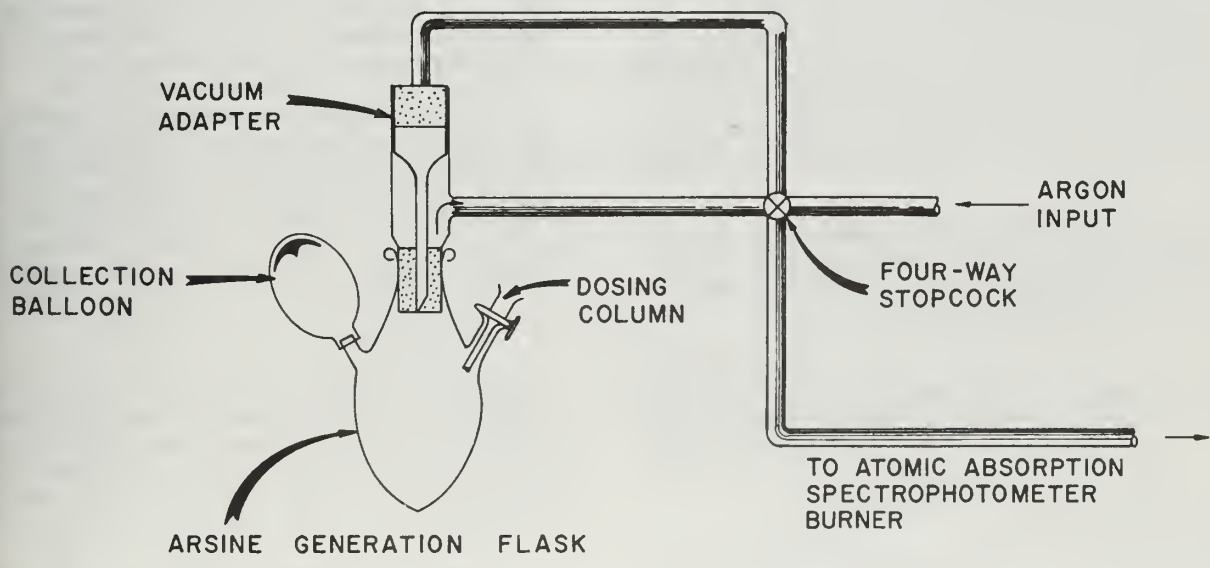


Figure 33. Arsine generation apparatus.

Other reagent solutions were prepared fresh for each batch of samples.

Procedure

1. Set up the A.A. unit with the As hollow cathode lamp; start the deuterium background corrector and a chart recorder and let them warm for 15 to 20 minutes. Keep the following settings:
 - Wavelength - 193.7 Å
 - Slit setting - 4
 - Lamp current - 20 mA
 - Fuel (H₂) Flow - 20
 - Oxidant (Ar) Flow - 30
 - Concentration Mode - 0-10
 - Recorder Response - 2 or 3
 - Recorder Chart Speed - 20 mm/min.
2. Make the required connections for hydrogen as the other fuel and argon as the other oxidant in the burner control chamber. Connect the auxiliary argon (from the back of the burner control) to the four-way stopcock (refer to Figure 33) and connect the other side of the four-way stopcock from where the arsine and hydrogen gas is driven off to the auxiliary oxidant position in the burner-nebulizer assembly. The other two sides of the four-way stopcock are connected to the generation flask for introducing the carrier argon gas and to carry the arsine and hydrogen produced to the burner nebulizer assembly. This can be done by changing the stopcock to the purge position. Argon in the bypass position is used to zero the instrument. Push the zero button when the flame is on.
3. Pipette 20 ml of standard or sample digest in the generation flask. If the sample has a higher concentration of arsenic, take less aliquot.
4. Add hydrochloric acid in such a quantity that the solution becomes 4 normal (N) when diluted to 40 ml with distilled water.
5. Add 1 ml of 15 percent potassium iodide solution with a tip-up pipette or micro-pipette. Mix well.
6. Add 1 ml of 20 percent stannous chloride solution, mix well and allow the solution to stand 3 to 4 minutes.
7. Completely wipe off the inside of the generation flask where additions are made. Connect the generation flask to the assembly with four-way stopcock in a bypass position.
8. Add 1.5 g of zinc metal to the generation flask through the side-dosing column and *immediately close the dosing funnel stopcock*. Wait 4 to 5 minutes until reaction between zinc and hydrochloric acid is complete and all the arsenic present in the solution has turned to arsine gas.
9. After 4 to 5 minutes, activate the recorder chart, light the flame and, keeping argon in bypass position, zero the instrument.
10. When zero is recorded on the chart, change four-way stopcock 90° to purge position, allow the auxiliary argon to flow through the flask and carry the collected arsine into the burner. Record the peak, and when the recorder-pen comes to zero position, return the four-way stopcock to bypass position and turn off the flame. By turning off flame at this stage, considerable argon and hydrogen gas can be saved.

Standard and sediment-digest blanks were run several times, and the average value obtained was subtracted from the corresponding values of standards and samples.

The only danger in using this device is that, due to moisture, zinc particles stick to the surface of the stopcock of the reaction vessel or dosing column. This might permit leakage of arsine, which might be inhaled by an operator. To avoid this, dry the neck of the dosing column and generation flask completely by wiping with a Kimwipe. As a further precaution, a portable fume-hood was built over this device and connected to the laboratory exhaust hood system.

Figure 34 represents the working curve drawn from the plots obtained by running various standards. This curve was used to calculate the concentration of all samples. Various standards were run between the analyses to check the reproducibility, which was found to be very good (see Appendix H).

(c) CADMIUM, COPPER, LEAD, AND ZINC

Cadmium, copper, lead, and zinc were determined by direct aspiration of respective standards and setting the working curve on the AA instrument. The filtered digests of the samples were then aspirated, and concentrations were read directly on the digital readout screen. The deuterium background corrector was used for the analyses of cadmium, lead and zinc.

Because the total digestion technique was not sufficiently sensitive to analyze the low quantities of cadmium present in sediments, the acid extraction technique was used. The values from each of the digestion methods were quite comparable, indicating that practically all of the cadmium had gone into solution with the acid extraction technique.

The acid extractions of most of the stream sediment samples were analyzed for copper, lead, and zinc. The values obtained were compared with those obtained from the totally digested samples, and it was found that the samples digested by the extraction technique showed lower concentrations than samples digested by the total digestion technique; therefore, the digestion technique was used for copper, lead, and zinc.

(d) PHOSPHORUS

Phosphorus was determined with the x-ray spectrometer by using one gram of 230-mesh sample, mixing it with one gram of Whatman CF-11 cellulose powder, making pellets in Spex press and analysing with an EDDT crystal and Cr target x-ray beam. All the phosphorus results are corrected for the presence of calcium.

The procedure for phosphorus determination is a modification of the technique after Fabbi (1971). The clayey nature of the samples

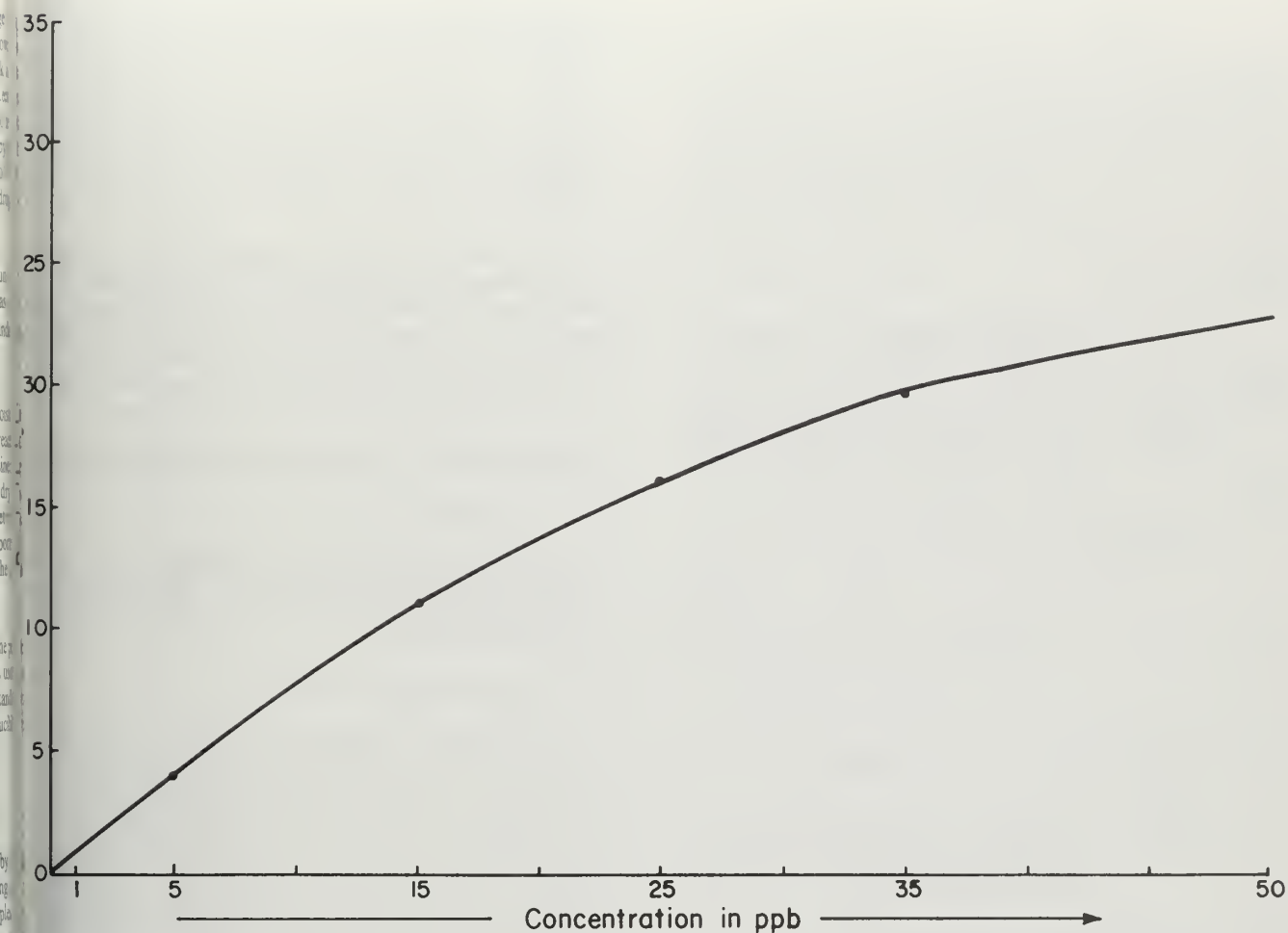


Fig. 34. Working curve for arsenic.

analyzed precluded extensive pulverizing sieving to 400 mesh as suggested by Fabbi.

1. Grind the sample for two minutes in Model #3800 Pitchford Pica Blender Mill, using stainless steel cylinders, stainless steel end buttons, two 15-mm stainless steel balls, and two aluminum end caps with four rubber 'O' rings. Fill each vial approximately $\frac{1}{3}$ full (~10 gm of less than #10-sieve material).
2. Split about $\frac{1}{4}$ of this sample for hand grinding to 230 mesh with agate mortar and pestle.
3. Dry the sample in the oven at 110° C.
4. Mix 1.0 gm of sample with 1.0 gm of Whatman CF-11 cellulose powder in a capped vial in a pica mill.
5. Prepare pellets, in duplicate, by filling Spex caps about half full of poly vinyl alcohol and other half with mixture of sample and cellulose, using a pressure of 16 tons per square inch.

The samples were then analyzed with a Cr Target x-ray tube, EDDT analyzing crystal, and a flow proportional counter at 1620 volts used in conjunction with a Phillips-Norelco vacuum spectrometer. X-radiation was generated at 40 kV and 37.5 mA on the target tube. A baseline setting of 8.5 volts and a window-setting of 9 volts was used to discriminate against most of the CaK interference. The remainder of this interference was subtracted in the following estimation:

1. Each sample was analyzed four times for at least 20 seconds and up to 100 seconds (for very low P samples) for counts between 8.5 volts and 17.5 volts. This would include all P and about 3 percent of the Ca counts due to a sample.
2. Each sample was analyzed four times for 10 to 20 seconds for counts beyond 8.5 volts. This includes essentially all P and all Ca counts.
3. About 3 percent of the Ca counts occur in the interval between 8.5 and 17.5 volts. This was determined from average data on a sample of powdered CaCO_3 and Cf-11 (1:1) run at the beginning and end of each day. The correction factor (RCa) was

calculated using the following formula:

$$R_{Ca} = \frac{\int_{8.5}^{17.5} CR}{\int_{8.5}^{0.0} CR - \int_{8.5}^{17.5} CR}$$

Where:

$$\int_{8.5}^{17.5} CR = \text{counts per second between 8.5 and 17.5 volts for } CaCO_3$$

$$\int_{8.5}^{0.0} CR = \text{counts per second greater than 8.5 volts for } CaCO_3$$

4. The following was used to obtain Ca-corrected values for P:

$$CR_P = \int_{8.5}^{17.5} CR - \left[R_{Ca} \left(\int_{8.5}^{0.0} CR - \int_{8.5}^{17.5} CR \right) \right]$$

Where:

CR_P = corrected count rate for phosphorus

$$\int_{8.5}^{17.5} CR = \text{counts per second between 8.5 and 17.5 volts for the unknown or standard rock sample (PHA on "diff")}$$

R_{Ca} = correction factor for Ca (see above)

$$\int_{8.5}^{0.0} CR = \text{counts per second beyond 8.5 volts for the unknown or standard rock sample (PHA on "integral")}$$

5. A standard high-phosphate sample was counted before and after each set of unknown samples. A fixed position (no. 2) was used to eliminate orientation variability between runs. Standard rocks were run in the second fixed position (no. 4). Instrumental drift was eliminated from the data by using the ratio method. Count rates of unknown samples were first corrected for Ca interference, then divided by the corrected count rate for the high-phosphate standard. This standard was corrected in two ways: (a) the regular Ca interference was subtracted, and (b) interpolations of data at the beginning and end of each run were used as divisors to get ratio comparisons. (For example, if the Ca-corrected count rate for the standard was 2800 cps at the beginning of a run, and 2600 cps at the end, the count rates for the three unknowns would be divided by 2750, 2700, and 2650 cps, respectively.)

PREPARATION OF THE HIGH PHOSPHATE STANDARD

The high-phosphate standard was prepared by mixing Florida phosphate (National Bureau of Standards Sample 120a) and Cf-11 cellulose powder and comparisons were made. During ap-

proximately two weeks of continuous use, this standard gave about 40 percent in x-ray intensity. Apparently, the cellulose was partially destroyed by the x-ray beam. Similar change also observed on another specimen which increased the intensity about 15 percent in 3 days. The cellulose destruction probably depends on the number of hours of exposure; the change in intensity is not gradual, so a correction for this change could be made.

A new standard ("A") was prepared by mixing 1.0 gm Florida Phosphate (National Bureau of Standards Sample 120a) with 1.0 gm of a clayey sediment (11/73). The clayey material acted as an excellent binder, and no destruction or change in intensity was observed in 4 weeks of continuous usage. A duplicate sample ("B"), which had received very little x-radiation, gave identical results before and after this period.

PREPARATION OF THE STANDARD WORKING CURVE

A. Standards with 0 to 0.5% P_2O_5

Standard rocks G-2, GSP-1, AGV-1, BCR-1, SY-1, T-1, were mixed with CF-11 cellulose powder (1:1). These were compared to the high-phosphate standard "A" to obtain a curve in the range 0 to 0.5% P_2O_5 .

B. Standards with 5 to 35% P_2O_5

Florida phosphate (National Bureau of Standards 120a) was mixed with reagent grade $CaCO_3$ in various proportions. The amount of each of these was then mixed with CF-11 cellulose powder (1:1) to prepare a pellet. The standards were labeled P-10 (50% 120a + 50% CF-11), P-8 (40% 120a + 50% $CaCO_3$ + 50% CF-11), P-6, (30% 120a + 20% $CaCO_3$ + 50% CF-11), P-4 (20% 120a + 30% $CaCO_3$ + 50% CF-11), P-2 (10% 120a + 40% $CaCO_3$ + 50% CF-11), and P-0 (50% $CaCO_3$ + 50% CF-11). These were then compared to the high-phosphate standard "A", as were all other samples.

Samples with unknown P_2O_5 concentrations were then compared to these two curves. For unknown samples with values between 0.5 and 5%, a curve was prepared by interpolation of data from the two standard curves.

CALCULATOR PROGRAMS FOR XRF ANALYSIS

The Commodore programming calculator was used to calculate the data. It takes about 2 hours to calculate data generated in 6 hours of x-ray operation. The five programs are as follows:

1. Calculate the average count rate.

Enter counting time, CR_1 , CR_2 , CR_3 , CR_4 ; record answer in "Avg." Column of XRF data sheet. Program Code:

MMM,N, 0.4, IV, 2 1/4, W, AC, 42. 6. 26. 26. 26. + 93
7393. 437., R, AC, 20, 1, 2, 3, 4 Ans. 2.

2. Calculate R_{Ca} from "diff" and "integral" data for sample P-0 run at beginning and end of the day's run.

Enter $\int_{8.5}^{17.5} CR$ and $\int_{8.5}^{0.0} CR$, record

R_{Ca} and average the two values. Program Code:

5, W, AC, 42. 6. 23. 4363. 493. 63 + 7., R, AC, 50, 2000, Ans.: 0.02564

3 Calcium correction.

Enter R_{Ca}, enter 8.5, 17.5 CR, 8.5, 0.0, and record "corrected cps" CR

Program Code:

R_a, IV, 2 1/4, W, AC, . 6. 23. 4383. 72362. + 3.423. 637., 30, 5000, Ans.: 2936

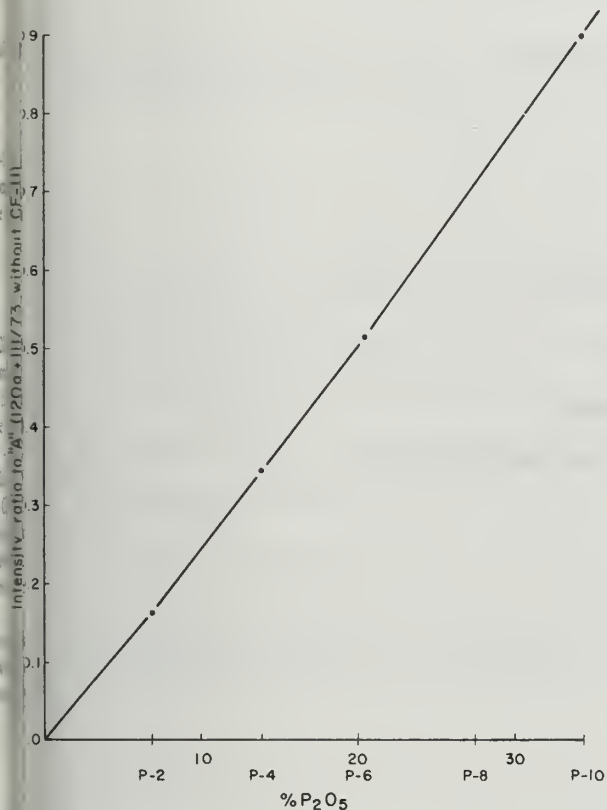


Figure 35. Working curve for P₂O₅ (high phosphate).

4. Drift correction.

Enter "corrected cps" for first or last analysis of an individual run, whichever is highest. Record first value under "cps drift" for first unknown if the first "B" corrected "cps" value was larger than the last. Record the first value under the third unknown if drift resulted in an increase in "corrected cps" of the "B" standard. Program Code:

4, IV, O 1/4, W, AC, 42. 3. 426. 393. 7362. 3.+ 423. 636. 3. 636. 3. 637., R, AC, 280, 260, Ans.: 275, 270, 265

5. Calculation of sample to standard ratio.

For each unknown, enter the "corrected cps" and then it's adjacent "cps drift." Record the sample to standard ratio under "sam/std." Plot on 0-0.5% or 0.5 to 35% P₂O₅ graphs. Program Code:

5 1/4, W, AC, 96.37., R, AC, 2, 3, Ans.:0.66667

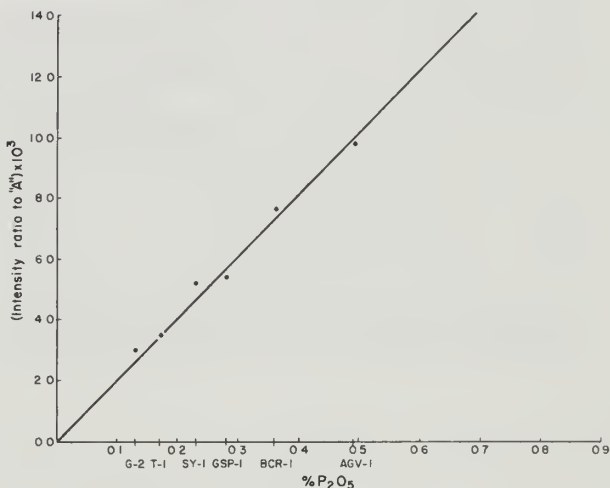


Figure 36. Working curve for P₂O₅ (low phosphate).

NOTES FOR APPENDICES F AND G

1. Detection limit in sample digests is as follows:
As - 1.0 ppb; Cd - 0.01 ppm; Cd (acid digest) - 0.01 ppm;
Cu - 0.1 ppm; Pb - 0.1 ppm; Hg - 0.1 ppb; Zn - 0.1 ppm.
2. Detection limit in samples is as follows:
As - 25.0 ppb; Cd - 0.25 ppm; Cd (acid digest) - 0.02 ppm;
Cu - 2.5 ppm; Pb - 2.5 ppm; Hg - 2.5 ppb; Zn - 2.5 ppm.
3. '0.0' means either the element is not detected or it is present in quantity less than the specified limit of detection.
4. 'N.D.' means not determined.
5. * Not used in statistical calculations.
6. (For Appendix G only). Detection limit for P is 0.01%.

Chemical Analyses of Stream Sediments

LAB. NO.	A5	CD	CU	P8	HG	ZN	LAB. NO.	A5	CD	CU	P8	HG	ZN
	(PPM)	(PPM)	(PPM)	(PPB)	(PPB)	(PPM)		(PPM)	(PPM)	(PPM)	(PPB)	(PPB)	(PPM)
209/72	0.6	0.2	8.0	3.0	10.0	10.0	279/72	0.8	0.0	3.0	0.0	13.0	12.0
210/72	2.0	3.0	0.0	0.0	15.0	32.0	280/72	1.4	0.0	0.0	3.0	5.0	19.0
211/72	3.9	5.0	10.0	0.0	28.0	32.0	281/72	3.0	0.0	3.0	5.0	18.0	9.0
212/72	0.0	10.0	23.0	15.0	512.0*	65.0	282/72	3.4	0.1	3.0	3.0	13.0	19.0
213/72	1.2	0.0	10.0	15.0	28.0	17.0	283/72	3.0	0.0	3.0	5.0	21.0	17.0
214/72	1.4	0.4	8.0	15.0	21.0	20.0	284/72	1.3	0.0	5.0	5.0	10.0	10.0
215/72	0.5	0.2	5.0	8.0	25.0	20.0	285/72	1.9	0.0	5.0	8.0	31.0	19.0
216/72	0.7	0.8	5.0	15.0	13.0	19.0	286/72	1.0	0.1	13.0	25.0	60.0	37.0
217/72	1.7	2.5	3.0	8.0	0.0	28.0	287/72	3.2	0.1	13.0	0.0	31.0	34.0
218/72	1.0	0.6	3.0	10.0	3.0	32.0	288/72	1.6	0.6	10.0	3.0	23.0	15.0
219/72	0.0	0.6	3.0	0.0	13.0	45.0	289/72	1.3	0.1	5.0	0.0	31.0	15.0
220/72	4.6	8.4	10.0	13.0	13.0	10.0	290/72	0.3	0.0	8.0	8.0	18.0	27.0
221/72	3.3	0.4	3.0	3.0	10.0	15.0	291/72	1.0	0.3	8.0	0.0	23.0	29.0
222/72	0.0	0.4	3.0	3.0	25.0	12.0	292/72	0.6	0.4	5.0	8.0	41.0	20.0
223/72	0.4	0.0	3.0	8.0	8.0	25.0	293/72	0.6	0.4	3.0	5.0	40.0	17.0
224/72	0.3	0.0	8.0	8.0	48.0	25.0	294/72	0.4	0.1	3.0	3.0	40.0	12.0
225/72	0.6	0.2	10.0	18.0	3.0	40.0	295/72	0.2	0.3	3.0	8.0	13.0	17.0
226/72	0.1	0.0	5.0	8.0	14.0	22.0	296/72	0.6	0.0	3.0	0.0	28.0	15.0
227/72	0.1	0.0	5.0	10.0	14.0	27.0	297/72	1.1	0.0	3.0	3.0	35.0	17.0
228/72	0.3	0.0	5.0	3.0	14.0	25.0	298/72	0.4	0.0	3.0	5.0	75.0	22.0
229/72	0.1	0.0	3.0	13.0	14.0	25.0	299/72	1.1	0.0	3.0	5.0	46.0	19.0
230/72	0.1	0.0	3.0	8.0	13.0	27.0	300/72	1.0	0.0	3.0	5.0	18.0	6.0
231/72	1.1	0.4	10.0	10.0	18.0	35.0	301/72	0.7	0.0	3.0	15.0	28.0	14.0
232/72	0.1	0.1	10.0	15.0	33.0	42.0	302/72	2.6	0.2	18.0	40.0	88.0	32.0
233/72	0.1	0.0	5.0	3.0	13.0	19.0	303/72	1.0	0.1	5.0	10.0	34.0	14.0
234/72	11.4	22.5	38.0	3.0	31.0	97.0	304/72	0.8	0.3	5.0	10.0	20.0	22.0
235/72	7.3	15.4	25.0	8.0	31.0	83.0	305/72	0.6	0.1	3.0	9.0	21.0	15.0
236/72	6.8	10.0	18.0	18.0	50.0	60.0	306/72	0.5	0.3	15.0	25.0	30.0	30.0
237/72	5.8	6.4	13.0	15.0	50.0	56.0	307/72	1.0	0.2	2.0	0.0	16.0	10.0
238/72	5.5	1.9	20.0	12.0	41.0	76.0	308/72	1.0	0.2	2.0	3.0	19.0	20.0
239/72	6.8	1.5	20.0	13.0	65.0	76.0	309/72	1.3	0.3	3.0	0.0	3.0	35.0
240/72	6.8	1.5	20.0	13.0	65.0	76.0	310/72	1.3	0.3	3.0	0.0	3.0	35.0
241/72	9.6	2.0	30.0	13.0	28.0	92.0	311/72	0.3	0.1	5.0	10.0	3.0	10.0
242/72	11.8	2.6	38.0	8.0	41.0	117.0*	312/72	1.3	0.1	3.0	10.0	25.0	17.0
243/72	19.1	15.4	18.0	8.0	38.0	74.0	313/72	2.5	0.1	8.0	8.0	28.0	40.0

LAB. NO.	A5	CD	CU	P8	HG	ZN	LAB. NO.	A5	CD	CU	P8	HG	ZN
	(PPM)	(PPM)	(PPM)	(PPB)	(PPB)	(PPM)		(PPM)	(PPM)	(PPM)	(PPB)	(PPB)	(PPM)
244/72	5.0	1.6	18.0	1.0	36.0	40.0	579/72	2.0	0.6	10.0	18.0	28.0	34.0
245/72	2.8	0.6	15.0	5.0	39.0	32.0	580/72	2.8	0.4	8.0	10.0	21.0	35.0
246/72	3.1	0.6	10.0	2.0	28.0	32.0	581/72	2.7	0.4	10.0	13.0	25.0	32.0
247/72	2.8	0.8	15.0	2.0	31.0	38.0	582/72	1.8	0.4	10.0	10.0	21.0	30.0
248/72	2.4	0.8	13.0	5.0	28.0	37.0	583/72	1.0	0.2	5.2	5.0	20.0	59.0
249/72	5.0	1.2	10.0	5.0	28.0	35.0	584/72	0.8	0.3	5.0	8.0	38.0	25.0
250/72	3.6	2.5	13.0	10.0	25.0	37.0	585/72	0.6	0.2	5.0	5.0	21.0	20.0
251/72	3.6	2.5	13.0	5.0	38.0	37.0	586/72	1.3	2.5	5.0	8.0	28.0	25.0
252/72	1.3	2.5	15.0	9.0	48.0	37.0	587/72	7.6	12.8	25.0	13.0	34.0	70.0
253/72	1.4	1.3	13.0	3.0	25.0	37.0	588/72	7.1	17.6	15.0	24.0	77.0	77.0
254/72	2.4	0.2	8.0	18.0	36.0	25.0	589/72	2.4	1.0	5.0	8.0	53.0	25.0
255/72	1.6	0.2	8.0	18.0	36.0	20.0	590/72	2.5	1.0	15.0	25.0	48.0	40.0
256/72	0.3	0.2	5.0	10.0	35.0	29.0	591/72	2.0	4.2	8.0	8.0	21.0	45.0
257/72	0.3	0.1	3.0	18.0	58.0	12.0	592/72	1.2	0.3	3.0	5.0	31.0	25.0
258/72	0.3	0.3	16.0	15.0	29.0	42.0	593/72	1.4	9.1	5.0	5.0	31.0	52.0
259/72	2.3	0.5	5.0	3.0	36.0	36.0	594/72	5.0	8.0	18.0	13.0	33.0	35.0
260/72	0.1	0.2	5.0	15.0	33.0	36.0	595/72	2.6	5.0	8.0	13.0	35.0	35.0
261/72	3.0	0.1	5.0	18.0	33.0	52.0	596/72	2.2	0.2	8.0	13.0	58.0	25.0
262/72	0.4	0.2	8.0	0.0	40.0	52.0	597/72	1.8	0.1	10.0	6.0	31.0	22.0
263/72	2.6	0.0	3.0	0.0	21.0	17.0	598/72	2.6	0.5	13.0	12.0	46.0	35.0
264/72	0.6	0.2	5.0	8.0	14.0	20.0	599/72	2.6	0.3	13.0	13.0	51.0	31.0
265/72	0.5	0.1	8.0	8.0	35.0	34.0	600/72	2.5	0.5	13.0	13.0	51.0	31.0
266/72	1.3	0.1	3.0	8.0	28.0	14.0	601/72	2.5	0.5	13.0	15.0	31.0	30.0
267/72	0.6	0.0	3.0	0.0	10.0	16.0	602/72	3.2	0.3	18.0	15.0	31.0	30.0
268/72	0.6	0.0	3.0	5.0	25.0	27.0	603/72	1.6	0.2	18.0	20.0	75.0	40.0
269/72	1.1	0.1	5.0	8.0	38.0	27.0	604/72	3.2	0.1	10.0	23.0	88.0	27.0
270/72	0.8	0.0	3.0	3.0	19.0	15.0	605/72	1.6	0.3	5.0	13.0	15.0	12.0
271/72	0.4	0.0	3.0	8.0	25.0	15.0	606/72	2.1	0.3	5.0	18.0	13.0	10.0
272/72	0.4	0.0	3.0	8.0	10.0	17.0	607/72	2.8	2.5	10.0	23.0	19.0	40.0
273/72	0.1	0.0	3.0	5.0	13.0	15.0	608/72	3.8	0.2	5.0	18.0	10.0	15.0
274/72	0.8	0.1	5.0	8.0	25.0	27.0	609/72	1.3	0.2	3.0	10.0	3.0	9.0
275/72	1.0	0.0	5.0	10.0	20.0	25.0	610/72	1.6	0.4	3.0	13.0	0.0	10.0
276/72	2.2	0.1	3.0	8.0	18.0	15.0	611/72	0.5	0.4	5.0	8.0	8.0	0.0
277/72	2.3	0.0	6.0	10.0	28.0	30.0	612/72	2.0	2.5	3.0	10.0	0.0	20.0
278/72	1.8	0.0	5.0	8.0	15.0	15.0	613/72	7.8	12.2	15.0	20.0	21.0	65.0

* Not used in statistical calculations.

APPENDIX G
Chemical Analyses of Bedrocks
and Some Stream Sediments

LAH. NO.	AS	CD	CU	PB	HG	P	ZN	LAH. NO.	AS	CD	CU	PB	HG	P	Z	
 (PPM) (PPM)							
					(PPB)	(%)	(PPM)						(PPB)	(%)	(P)	
93/73	2.5	0.5	30.0	22.3	42.5	N.D.	26.0	163/73	19.3	8.0	37.5	20.0	0.0	0.32	4	
94/73	4.0	6.0	17.5	19.0	0.0	N.D.	62.0	164/73	9.8	2.9	15.0	18.8	45.0	N.D.	3	
95/73	11.5	8.4	27.5	18.8	15.0	N.D.	46.0	165/73	17.5	0.6	35.0	22.5	0.0	N.D.	3	
96/73	12.5	28.0	25.0	22.5	30.0	0.16	114.0	166/73	5.3	0.6	20.0	16.5	2.5	N.D.	1	
97/73	14.0	21.5	37.5	20.8	15.0	0.36	72.0	167/73	19.5	348.0	122.5	24.0	17.5	11.54	35	
98/73	10.0	17.2	27.5	27.0	0.0	0.31	53.0	168/73	31.5	348.0	162.5	27.0	140.0	15.01	33	
99/73	12.5	17.5	25.0	17.5	42.5	0.17	56.0	169/73	22.0	3.8	37.5	18.8	0.0	N.D.	3	
100/73	11.5	3.6	20.0	20.0	7.5	N.D.	34.0	170/73	12.5	11.0	32.5	16.8	0.0	0.24	5	
101/73	27.0	90.0	110.0	27.5	7.5	4.42	214.0	171/73	18.8	52.0	74.0	27.0	0.0	1.94	14	
102/73	7.0	9.6	20.0	24.8	8.8	0.54	41.0	172/73	1.5	5.0	12.5	23.0	5.0	N.D.	3	
103/73	8.5	3.6	17.5	23.8	0.0	N.D.	47.0	173/73	10.5	6.5	25.0	22.0	0.0	0.31	4	
104/73	6.0	1.4	27.5	21.0	22.5	N.D.	23.0	174/73	0.8	0.1	32.8	20.8	11.3	N.D.	2	
105/73	3.0	1.0	17.5	19.8	15.0	N.D.	14.0	175/73	9.0	5.3	20.0	18.3	0.0	N.D.	4	
106/73	3.0	3.0	22.5	17.5	0.0	N.D.	26.0	176/73	0.0	0.2	5.0	15.5	0.0	N.D.	0	
107/73	3.5	11.0	25.0	22.5	5.0	0.11	58.0	177/73	27.0	150.0	124.5	22.5	0.0	9.21	23	
108/73	2.3	1.2	22.5	24.5	30.0	N.D.	22.0	178/73	5.8	18.6	15.0	18.0	0.0	0.57	6	
109/73	5.3	9.6	20.0	18.5	7.5	0.18	43.0	179/73	17.0	10.0	22.5	18.0	5.0	0.51	5	
110/73	4.8	1.0	15.0	15.0	7.5	N.D.	17.0	180/73	2.6	0.8	3.0	12.8	5.0	N.D.	0	
111/73	38.5	22.6	47.5	28.0	7.5	0.52	100.0	181/73	65.0	14.0	47.5	35.0	31.3	0.57	8	
112/73	20.8	20.0	25.0	18.8	0.0	0.58	85.0	182/73	5.8	9.0	22.5	18.5	0.0	0.60	5	
113/73	11.5	1.6	22.5	19.8	8.8	N.D.	26.0	183/73	4.8	1.8	10.0	23.0	5.0	N.D.	2	
114/73	17.0	3.6	30.0	21.0	0.0	N.D.	25.0	184/73	7.0	6.0	45.0	18.8	0.0	N.D.	6	
115/73	29.5	96.0	130.0	26.5	27.5	4.55	235.0	185/73	4.8	1.0	25.0	15.8	0.0	N.D.	2	
116/73	32.5	50.0	57.5	28.8	7.5	1.98	154.0	186/73	14.8	0.8	20.0	24.3	2.5	N.D.	1	
117/73	16.5	6.0	20.0	17.8	0.0	N.D.	36.0	187/73	2.1	0.2	7.5	18.0	0.0	N.D.	0	
118/73	4.5	15.0	15.0	19.3	0.0	0.35	50.0	188/73	14.8	10.0	30.0	18.0	45.0	0.17	6	
119/73	9.5	1.4	25.0	18.8	0.0	N.D.	24.0	189/73	4.8	1.0	27.5	13.8	5.0	N.D.	2	
120/73	6.0	3.6	25.0	21.3	0.0	N.D.	24.0	190/73	4.8	1.0	26.3	20.0	77.5	N.D.	0	
121/73	3.4	38.5	7.5	27.8	0.0	1.48	107.0	191/73	1.4	0.1	23.0	28.0	0.0	N.D.	1	
122/73	6.5	1.2	22.5	18.8	0.0	N.D.	19.0	192/73	17.5	1.1	45.0	20.0	21.3	N.D.	5	
123/73	20.8	3.6	17.5	19.8	60.0	N.D.	32.0	193/73	3.2	0.3	5.0	15.0	0.0	N.D.	0	
124/73	5.1	5.0	10.0	19.3	72.5	N.D.	24.0	194/73	4.8	0.6	2.5	13.8	0.0	N.D.	0	
125/73	11.4	5.0	22.5	20.0	72.5	N.D.	52.0	195/73	8.0	0.6	25.0	11.3	0.0	N.D.	0	
126/73	7.2	0.4	17.5	28.3	0.0	N.D.	10.0	196/73	20.0	3.0	24.0	22.5	77.5	N.D.	5	
127/73	5.3	1.0	30.0	19.5	20.0	N.D.	21.0	197/73	3.0	2.4	7.5	15.0	0.0	N.D.	0	

LAH. NO.	AS	CD	CU	PB	HG	P	ZN	LAH. NO.	AS	CD	CU	PB	HG	P	Z	
 (PPM) (PPM)							
					(PPB)	(%)	(PPM)						(PPB)	(%)	(P)	
128/73	15.0	12.0	22.5	22.5	0.0	0.13	74.0	198/73	8.5	3.1	22.0	10.0	0.0	N.D.	0	
129/73	20.0	20.0	21.3	21.3	12.5	0.57	90.0	199/73	5.3	3.0	10.0	15.0	0.0	N.D.	0	
130/73	9.5	19.4	15.0	29.3	0.0	N.D.	58.0	200/73	10.5	10.0	15.0	18.8	5.0	0.06	0	
131/73	72.0	4.0	27.5	47.8	160.0	N.D.	48.0	201/73	6.3	7.3	25.0	15.5	2.5	0.07	0	
132/73	5.1	1.0	20.0	21.8	0.0	N.D.	26.0	202/73	7.0	7.6	12.5	15.0	0.0	0.07	0	
133/73	4.8	3.8	27.5	25.0	5.0	N.D.	28.0	203/73	12.8	10.0	22.5	21.8	40.0	0.07	0	
134/73	5.3	2.4	30.0	23.3	0.0	N.D.	31.0	204/73	1.0	0.5	12.5	14.0	138.0	N.D.	0	
135/73	11.8	3.0	45.0	21.8	5.0	N.D.	54.0	205/73	13.3	16.6	22.5	22.5	40.0	0.07	0	
136/73	10.0	6.0	32.5	21.8	5.0	N.D.	64.0	206/73	6.3	32.2	33.3	17.5	0.0	0.99	0	
137/73	3.2	0.2	12.5	20.0	5.0	N.D.	10.0	207/73	3.5	0.5	7.5	15.8	0.0	N.D.	0	
138/73	0.4	0.0	30.0	18.3	5.0	N.D.	10.0	208/73	4.3	0.5	20.0	27.8	70.0	N.D.	0	
139/73	2.5	0.0	7.5	16.8	15.0	N.D.	8.0	209/73	2.3	0.8	7.5	20.0	47.5	N.D.	0	
140/73	5.7	2.2	15.0	19.3	15.0	N.D.	30.0	210/73	3.2	5.0	7.5	16.3	0.0	N.D.	0	
141/73	2.3	0.3	17.5	16.0	10.0	N.D.	16.0	211/73	8.0	3.0	17.5	18.0	62.5	N.D.	0	
142/73	1.1	17.0	5.8	20.0	25.0	0.30	58.0	212/73	9.8	13.1	20.3	20.0	40.0	0.07	0	
143/73	7.0	6.4	17.3	30.0	0.0	N.D.	48.0	213/73	7.0	4.0	10.0	16.5	47.5	N.D.	0	
144/73	2.1	1.0	10.0	16.3	10.0	N.D.	32.0	214/73	7.5	0.5	10.0	16.3	0.0	N.D.	0	
145/73	9.0	1.8	12.5	17.3	0.0	0.28	20.0	215/73	3.0	7.2	2.5	14.5	0.0	0.31	0	
146/73	4.3	5.0	25.0	19.5	0.0	N.D.	33.0	216/73	12.8	2.8	10.0	15.0	92.5	N.D.	0	
147/73	6.3	8.0	7.5	28.5	0.0	0.21	42.0	217/73	9.8	2.3	37.5	30.0	0.0	N.D.	0	
148/73	17.5	0.9	22.5	18.0	5.0	N.D.	25.0	218/73	12.3	2.0	15.0	18.8	0.0	N.D.	0	
149/73	17.0	14.0	37.5	22.5	5.0	0.08	58.0	219/73	10.0	10.6	20.0	15.0	0.0	0.37	0	
150/73	16.0	3.6	17.5	19.3	0.0	N.D.	38.0	220/73	9.8	0.1	7.5	23.0	0.0	N.D.	0	
151/73	5.3	6.0	25.0	17.0	0.0	N.D.	39.0	221/73	4.3	0.8	18.5	21.5	7.5	N.D.	0	
152/73	14.3	10.0	30.0	24.5	57.5	N.D.	77.0	222/73	12.8	1.2	9.3	22.0	0.0	N.D.	0	
153/73	5.1	8.0	20.0	19.8	5.0	0.26	44.0	223/73	6.3	0.2	13.8	21.0	0.0	N.D.	0	
154/73	9.0	1.0	12.5	16.5	50.0	N.D.	19.0	224/73	14.3	1.0	10.0	20.8	0.0	N.D.	0	
155/73	19.3	32.8	32.5	25.3	5.0	1.22	118.0	225/73	8.5	0.3	7.5	18.8	0.0	N.D.	0	
156/73	10.0	15.4	25.0	18.8	0.0	0.14	55.0	226/73	12.3	0.3	7.0	16.8	30.0	N.D.	0	
157/73	14.3	10.0	25.0	16.0	5.0	0.07	62.0	227/73	7.0	0.0	12.8	20.0	55.0	N.D.	0	
158/73	8.5	5.7	23.0	15.0	0.0	N.D.	37.0	228/73	3.0	0.1	9.8	20.0	0.0	N.D.	0	
159/73	14.8	166.0	150.0	26.3	11.3	7.72	275.0	229/73	19.3	0.0	15.5	22.0	55.0	N.D.	0	
160/73	18.5	121.0	132.5	25.0	17.5	7.29	245.0	230/73	4.8	0.2	11.8	19.3	62.5	N.D.	0	
161/73	0.5	0.8	12.5	17.0	5.0	N.D.	21.0	231/73	2.6	0.2	8.0	19.0	0.0	N.D.	0	
162/73	27.5	27.6	57.5	24.5	0.0	0.33	103.0	232/73	2.6	0.4	7.5	17.0	40.0	N.D.	0	

APPENDIX H
Precision and Accuracy
of the
Analytical Techniques

The precision of the analytical techniques developed in this project was tested to determine the aggregate errors resulting from sample splitting, digesting, diluting, and analyzing by analytical instruments. Ten replications of samples 607/72 and 167/73 were digested and run as unknowns at various times during analyses. Similarly, N.B.S. 120a was digested in ten replications and run for phosphorous. The results of this precision test and the standard deviations are given in Table 9.

To check the accuracy of the method of analyses, U.S. Geological Survey standard rock samples G-2 and GSP-1 were digested

four times, and Canadian Association of Applied Spectroscopists standard rock sample Sulphide Ore was digested two times and analyzed several times as the unknown with the other samples. Unfortunately, these rock standards did not cover the accuracy of cadmium determination. However, cadmium was analyzed two times from two separate digests for each sample. The results seem to be in good agreement with each other, and the reproducibility seems to be very good. As a whole, the precision is sufficient for these samples, and the accuracy of the technique is very good.

Table 9. Precision tests for ten replications of samples 607/72, 167/73, and N.B.S. 120a.

Element	n	#607/72 (Stream Sediment)		#167/73 (Phosphatic Pellets)		N.B.S. 120 a (Phosphatic Limestone)	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
		x	s	x	s	x	s
As	10	3.8 ppm	3.6 ppm	19.5 ppm	3.2 ppm	-	-
Cd	10	2.5 ppm	1.2 ppm	348.0 ppm	1.0 ppm	-	-
Cu	10	10.0 ppm	3.7 ppm	122.5 ppm	2.7 ppm	-	-
Pb	10	23.0 ppm	2.4 ppm	24.0 ppm	1.5 ppm	-	-
Hg	10	19.0 ppb	10.8 ppb	17.5 ppb	8.5 ppb	-	-
P	10	-	-	-	-	16.42%	0.12%
Zn	10	40.0 ppm	2.1 ppm	11.5 ppm	2.0 ppm	-	-

Table 10. Accuracy of arsenic, copper, lead, mercury, and zinc analyses.

Standard Rocks	Reference	As (ppm)		Cu (ppm)		Pb (ppm)		Hg (ppb)		Zn (ppm)	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
U.S.G.S. G-2	Majmundar ^{1/}	1.2(8)	0.9-1.5	13(8)	10-15	27(8)	24-33	46(8)	46-47	80(8)	74-84
	Flanagan ^{2/}	0.98(4)	0.8-1.2	11(24)	<2-17	29(18)	15-43	47(5)	29-50	83(15)	42-96
U.S.G.S. GSP-1	Majmundar	1.35(6)	1.0-1.75	32(8)	28-36	48(8)	42-58	17(8)	16-17	110(8)	96-120
	Flanagan	1.25(4)	1.1-1.4	34(25)	15-54	51(19)	14-80	17(5)	15-41	114(16)	54-120
C.A.A.S. Sulphide Ore	Majmundar	300(4)	275-350	8273(6)	8180-8360	256(13)	236-274	NO DATA		221(13)	202-240
	Webber ^{3/}	424(8)	250-500	8291(16)	4000-12000	248(11)	200-310	NO DATA		298(8)	160-320

Notes: 1. Number in parentheses represents number of readings. Four separate digestions were made for USGS G-2 and GSP-1, and two separate digestions were made for C.A.A.S. Sulphide Ore.
2. Flanagan, F.J. (1973).
3. Webber, G.R. (1965).

APPENDIX I

Statistical Treatment of Data

The results of chemical analyses of arsenic, cadmium, copper, lead, mercury, phosphorous, and zinc are recorded in Appendices F and G. The very highly anomalous values, which are marked with an asterisk (*) in the tables, were considered to be random and were not considered in statistical calculations. All the calculations are based on the 201 stream sediment and 259 bedrock samples. The results of analyses of cadmium and phosphorous in samples from localities other than those in the area under investigation is given in Table 6.

These data were plotted on the maps at the respective sample locations by plotting one element on each map (Figures 5 through 17).

Histograms clearly illustrate the effect of the detection limit of the analytical method. However, histograms can be misleading because they are strongly affected by slight changes in class intervals. Histograms and cumulative frequency curves, drawn from the same data, can be compared easily. Cumulative frequency distribution curves were drawn for all the elements analysed in the present study by the graphical methods described by Lepeltier (1969). Frequencies were calculated from lowest to highest values, plotted against concentration on log-probability paper (Figures 37 through 49), and then used to calculate statistical parameters (Table 11). Histograms were constructed (Figures 50 through 62) plotting the percentage of frequencies against element concentration on 2- or 3-cycle, semi-log paper. Statistical parameters were compared with crustal and soil abundances.

There are two reasons for drawing the cumulative frequency curve: to check whether it fits a lognormal distribution and, if it does, to estimate the basic parameters, background (b), coefficients of deviation (s' , s) and threshold level (t). The background gives the average concentration levels of the elements in a given setting. A single straight line shows a single population, lognormally distributed. In such a case, the background concentration is indicated by the intersection of the straight line with the 50 percent ordinate, illustrated in Figure 48 for zinc in stream sediment samples. In the case of a perfect frequency distribution curve, the background, calculated in this way, corresponds to the mode and median values and is the geometric mean of the results.

By projecting the intersection of the 84 percent ordinate with the straight line, a value is obtained which is divided by the geometric mean value to get the geometric deviation (s'). The logarithm of this value is the coefficient of deviation (s). Coefficient of deviation expresses the scatter of the values around (b) and corresponds to the spread of the values and their range, from the lowest to the highest.

After obtaining the background and coefficients of deviation the third important parameter, the threshold level (t), can be calculated by the following formula:

$\log t = (\log b) + 2s$, Where t is threshold level; b, the background, and s, the coefficient of deviation.

The threshold level represents an upper limit, above which the values are considered anomalous. This can be read directly from the graph as the abscissa of the intersection of the distribution line with the 97.5 percent ordinate. Values greater than this were considered anomalous.

The procedure for calculating the statistical parameters can be illustrated easily by taking the example of zinc in stream sediment samples. In this study, zinc represents the perfect lognormal distribution. The background calculated in this case corresponds to the mode and median values and is the geometric mean of the results. This geometric mean is considered to be more significant and a more stable statistic than the arithmetic mean. It is less subject to change with the addition of new data and less affected by high values. For example, the geometric mean of cadmium in bedrocks is 5.2, and the arithmetic mean is 27.2, which is greater than the threshold level. In the case of zinc, the geometric mean, calculated by the intersection of the straight line with the 50 percent ordinate, was 21.5 ppm Zn.

If (b) is the median value and (s) the standard deviation, then 68 percent of the population will fall between $b-s$ and $b+s$; and 97.5 percent of the population will fall between $b-2s$ and $b+2s$. As 68 percent of the population falls between $b-s$ and $b+s$, 32 percent of the population falls outside this limit (i.e. 16 percent of the values fall above $b+s$ and 16 percent below $b-s$). In Figure 48, the values $b-s$ and $b+s$ were obtained by projecting the intersection of straight line with the ordinate 16 percent and 84 percent on the abscissa. As all the frequency curves were drawn in logarithmic scale, the ratios were taken into consideration rather than the absolute values. Thus, points P (at 84 percent ordinate) and A were determined. OA is the geometrical expression of the deviation and is known as geometric deviation (s'), which is a factor obtained by dividing the value read at A by the value at O (1.86 in the case of zinc). Then dividing or multiplying the background value (21.5) by the geometric deviation (1.86), the upper and lower limits respectively of a range that encompasses 68 percent of the population were calculated as 11.5 to 40 ppm Zn. Further, dividing or multiplying by the squares of the geometric deviation provides a range encompassing 97.5 percent of the population and extending from 6.2 to 74 ppm Zn.

The coefficient of deviation (s) is 0.27, obtained by reading the logarithmic of geometric deviation (s'), 1.86 for zinc. The third important parameter, threshold level, is the function of (b) and (s). In case of symmetrical distribution (normal or log normal), 97.5 percent of the population falls between $b+2s$ and $b-2s$. Thus, this upper limit was read directly from the cumulative frequency curve as the abscissa of the intersection of the distribution line with 97.5 percent ordinate and was calculated by using the preceding formula. The threshold level for zinc was found to be 74 ppm Zn, taken from the curve as well as calculated from the formula.

In cases where a complex population was sampled (Figures 39 through 42, 46, and 47), there were two distinct straight lines with different slopes, one representing the lognormal population, the other the probable anomalous population. The thresholds

levels in such cases were taken at the break in slope. For example, in the case of Cd (in both, stream sediment and bedrock samples), the data show a positive skew in the direction of the high values, and the data for Cu (in stream sediment samples) show a negative skew in the direction of the low values. In such statistical studies the coefficients of deviation are very important. It is possible for two populations to have the same background, but they will have different threshold levels if their coefficients of deviation are different.

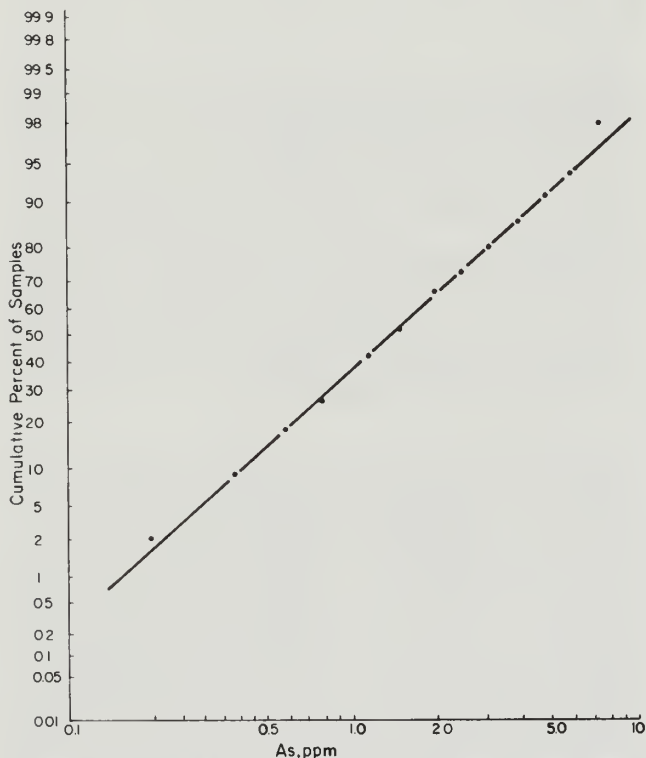


Figure 37. Cumulative frequency distribution for arsenic in stream sediments (N= 189).

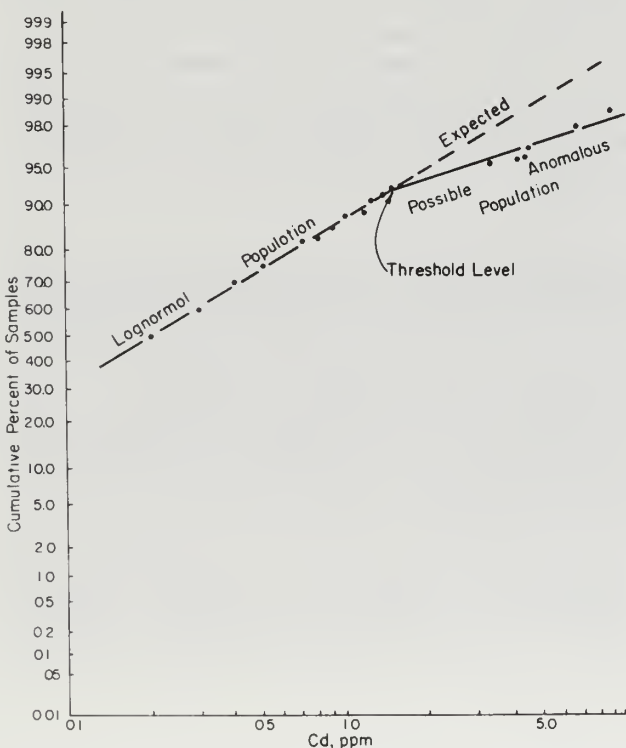


Figure 39. Cumulative frequency distribution for cadmium in stream sediments (N= 156).

In the case of Cd and Cu, the cumulative frequency distribution curves show two breaks, and the histograms give double peaks. This dual distribution suggests the presence of two distinct populations. These curves also could be interpreted by splitting the data at a value taken around the place where break occurred, separating the total population into two parts and drawing two separate curves. In such a procedure, the coefficients of deviation and threshold levels may be calculated separately for both populations.

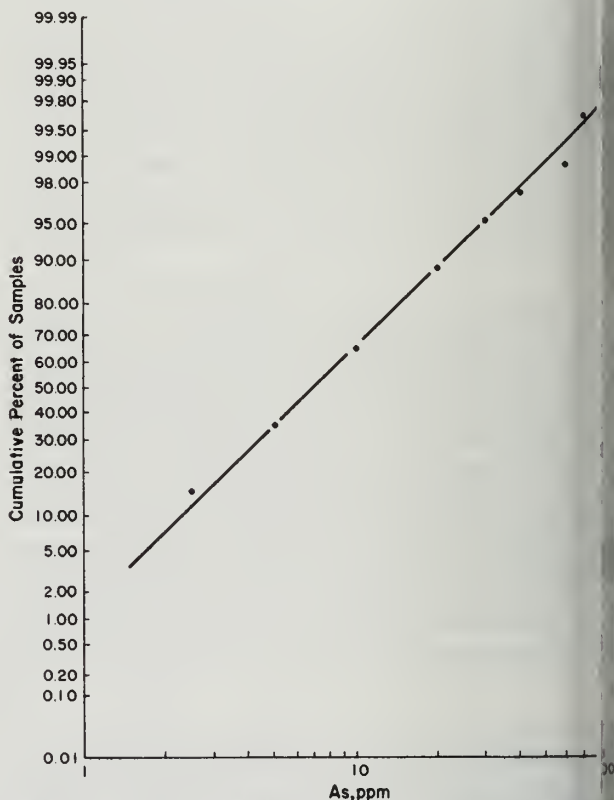


Figure 38. Cumulative frequency distribution for arsenic in bedrock (N= 258).

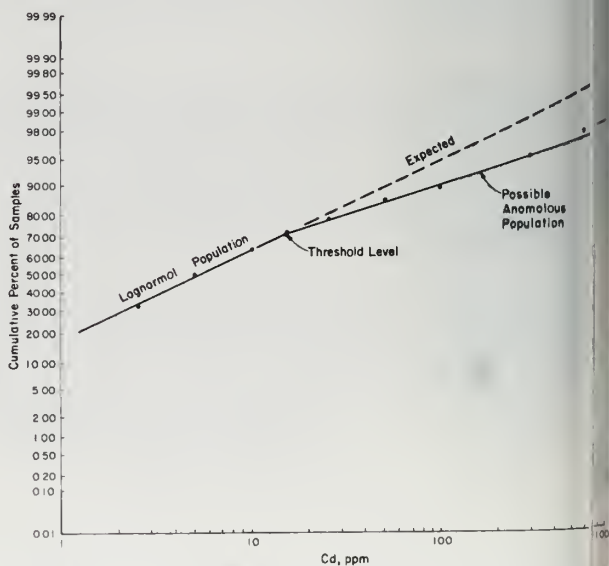


Figure 40. Cumulative frequency distribution for cadmium in bedrock (N= 235).

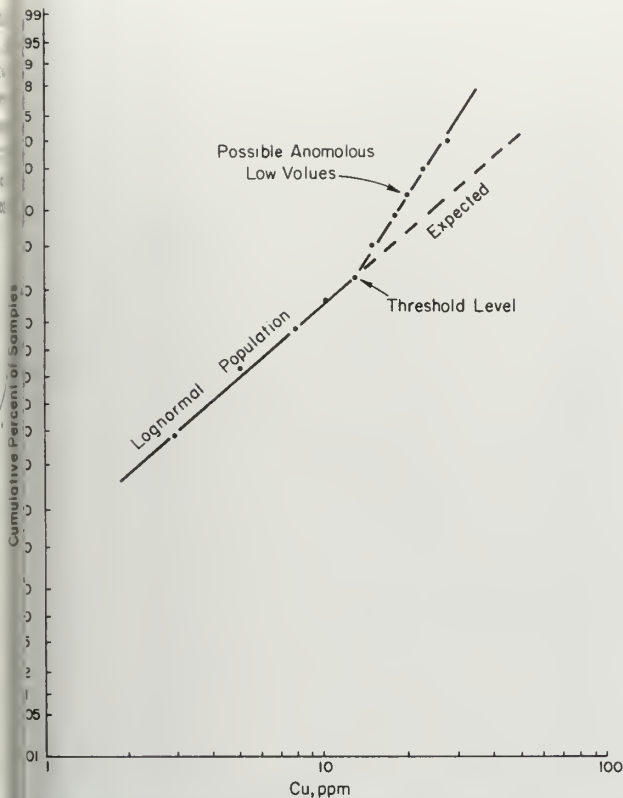


Fig. 41. Cumulative frequency distribution for copper in stream sediments (N= 189).

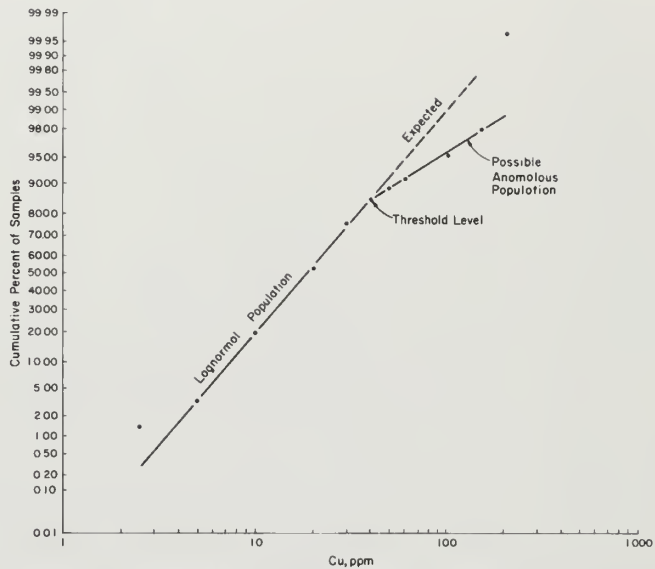


Figure 42. Cumulative frequency distribution for copper in bedrocks (N = 259).

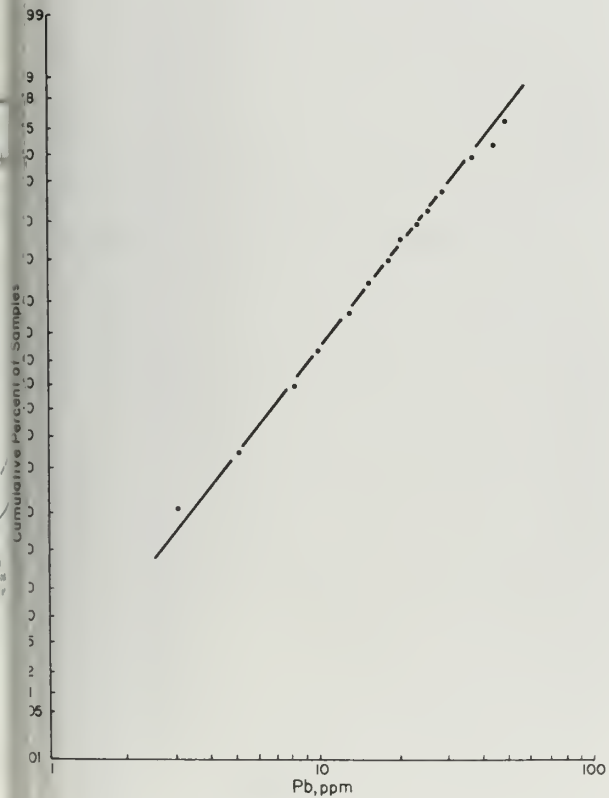


Fig. 43. Cumulative frequency distribution for lead in stream sediments (N= 167).

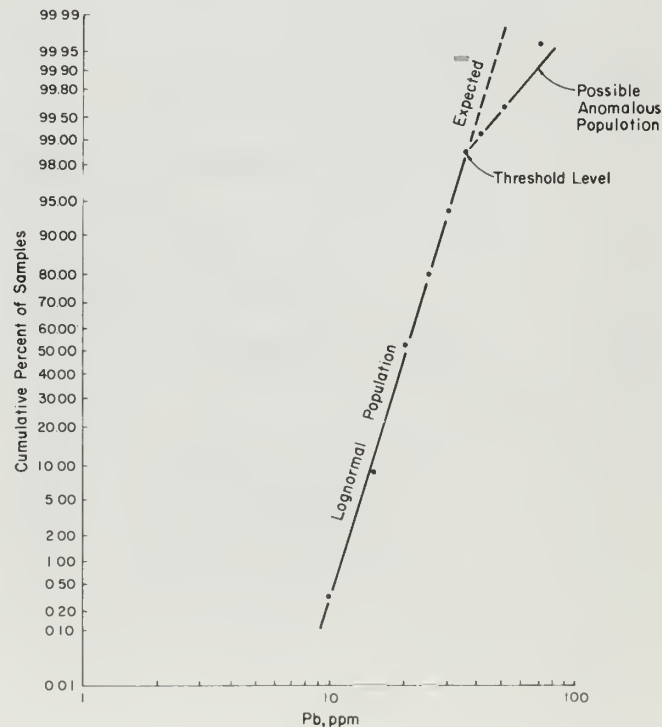


Figure 44. Cumulative frequency distribution for lead in bedrocks (N= 259).

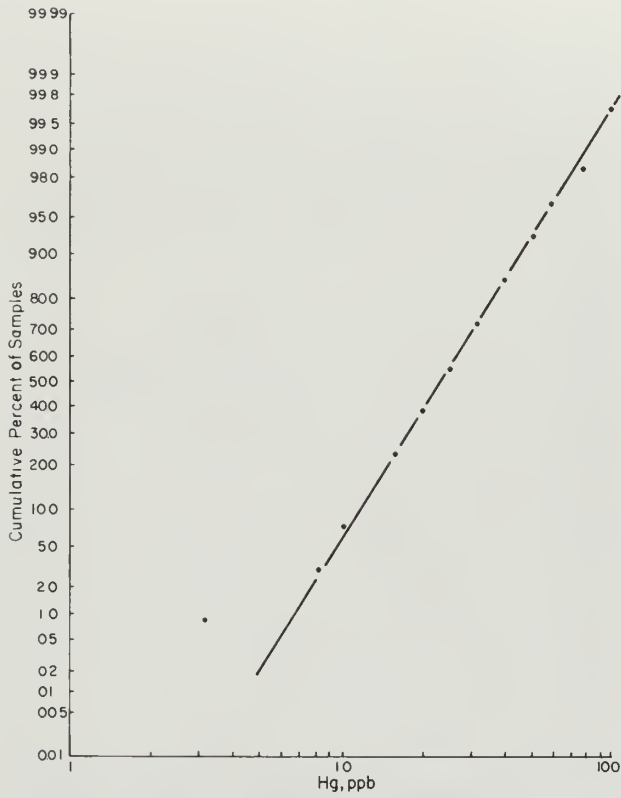


Figure 45. Cumulative frequency distribution for mercury in stream sediments (N= 153).

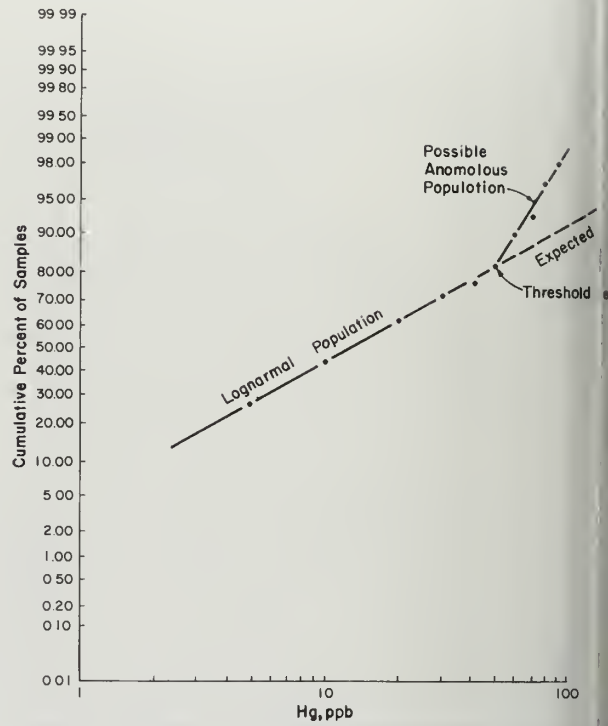


Figure 46. Cumulative frequency distribution for mercury in bedrock (N = 135).

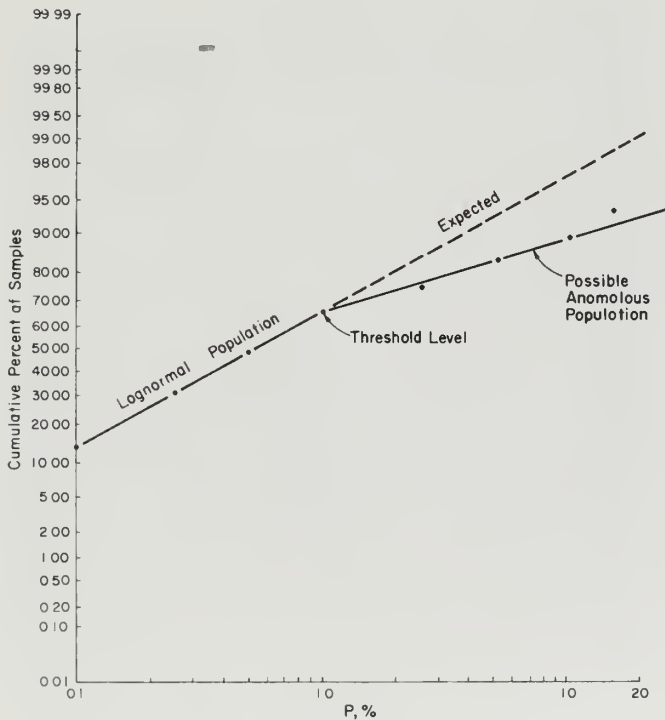


Figure 47. Cumulative frequency distribution for phosphorus in bedrocks (N = 97).

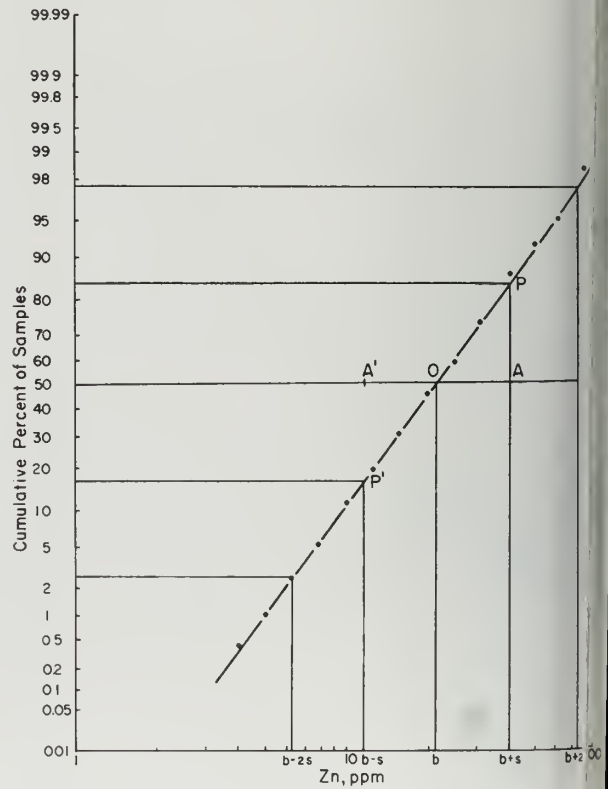


Figure 48. Cumulative frequency distribution for zinc in stream sediments (N= 198).

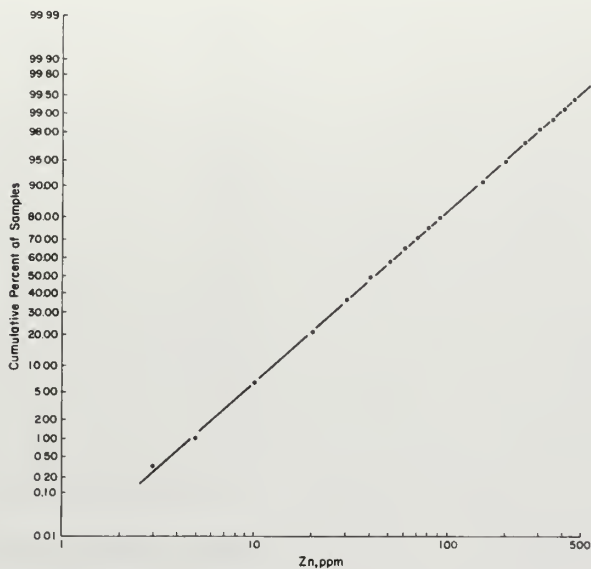


Figure 49. Cumulative frequency distribution for zinc in bedrocks (N= 259).

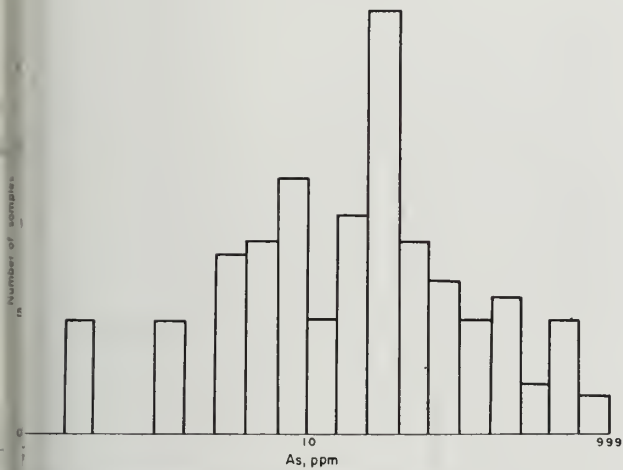


Figure 50. Histogram for arsenic in stream sediments.

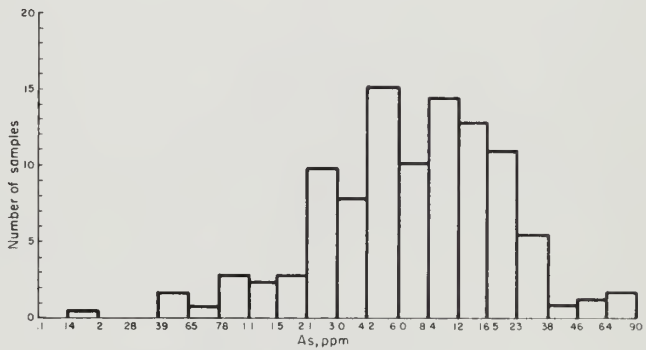


Figure 51. Histogram for arsenic in bedrocks.

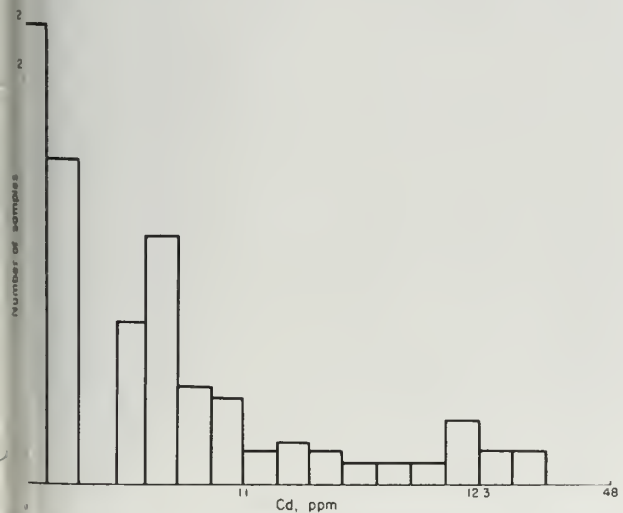


Figure 52. Histogram for cadmium in stream sediments.

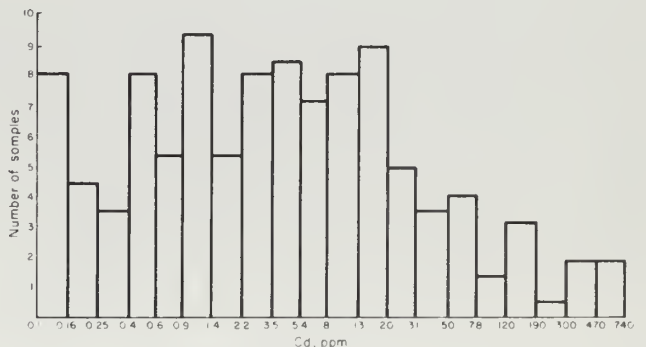


Figure 53. Histogram for cadmium in bedrocks.

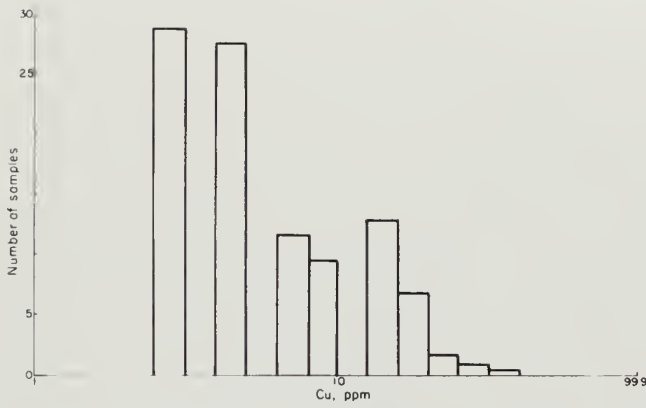


Figure 54. Histogram for copper in stream sediments.

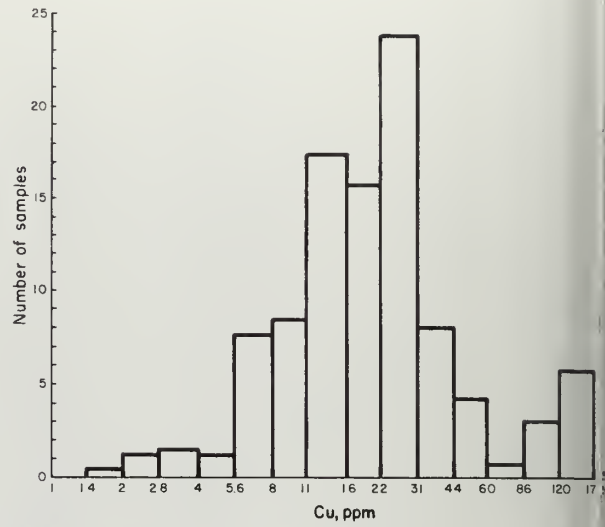


Figure 55. Histogram for copper in bedrocks.

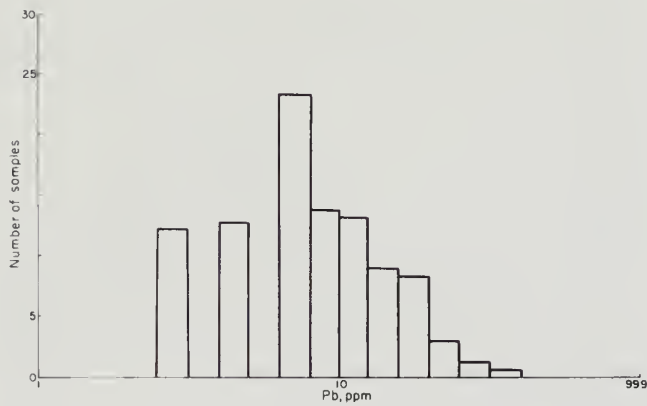


Figure 56. Histogram for lead in stream sediments.

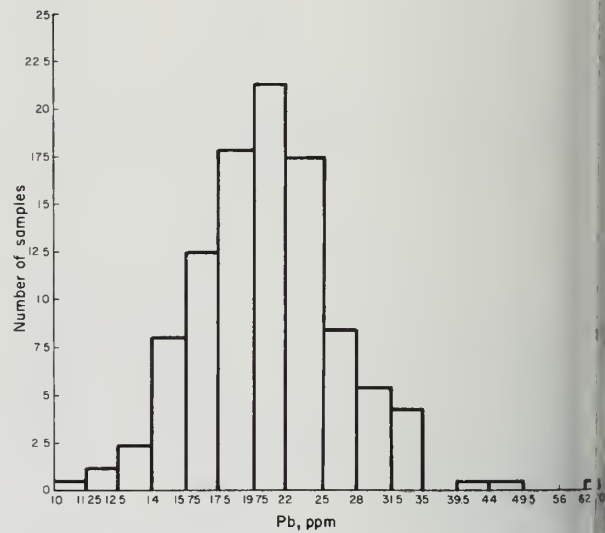


Figure 57. Histogram for lead in bedrocks.

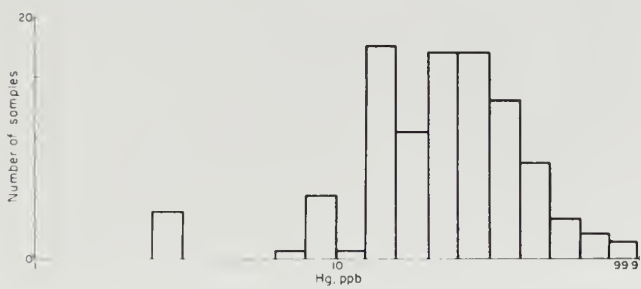


Figure 58. Histogram for mercury in stream sediments.

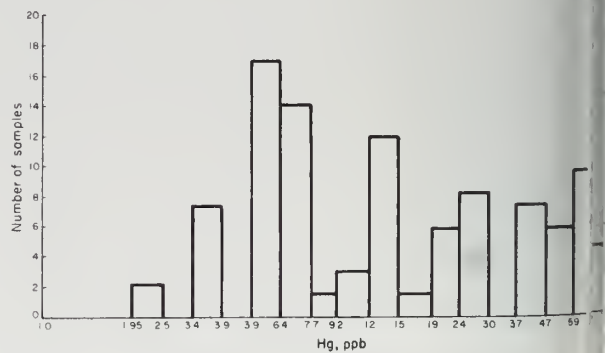


Figure 59. Histogram for mercury in bedrocks.

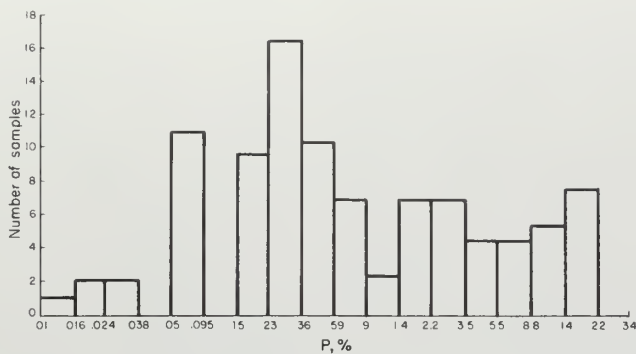


Figure 60. Histogram for phosphorus in bedrocks.

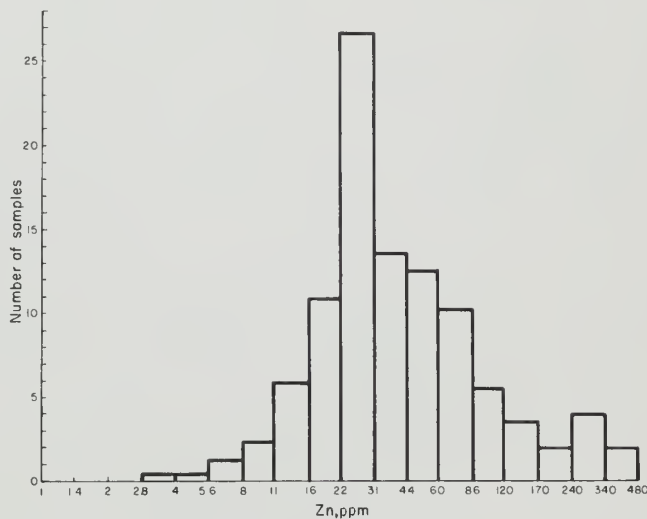


Figure 62. Histogram for zinc in bedrocks.

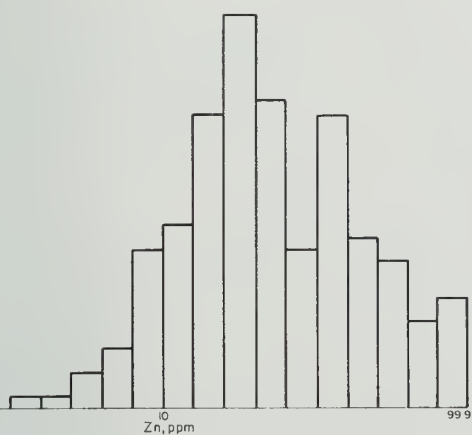


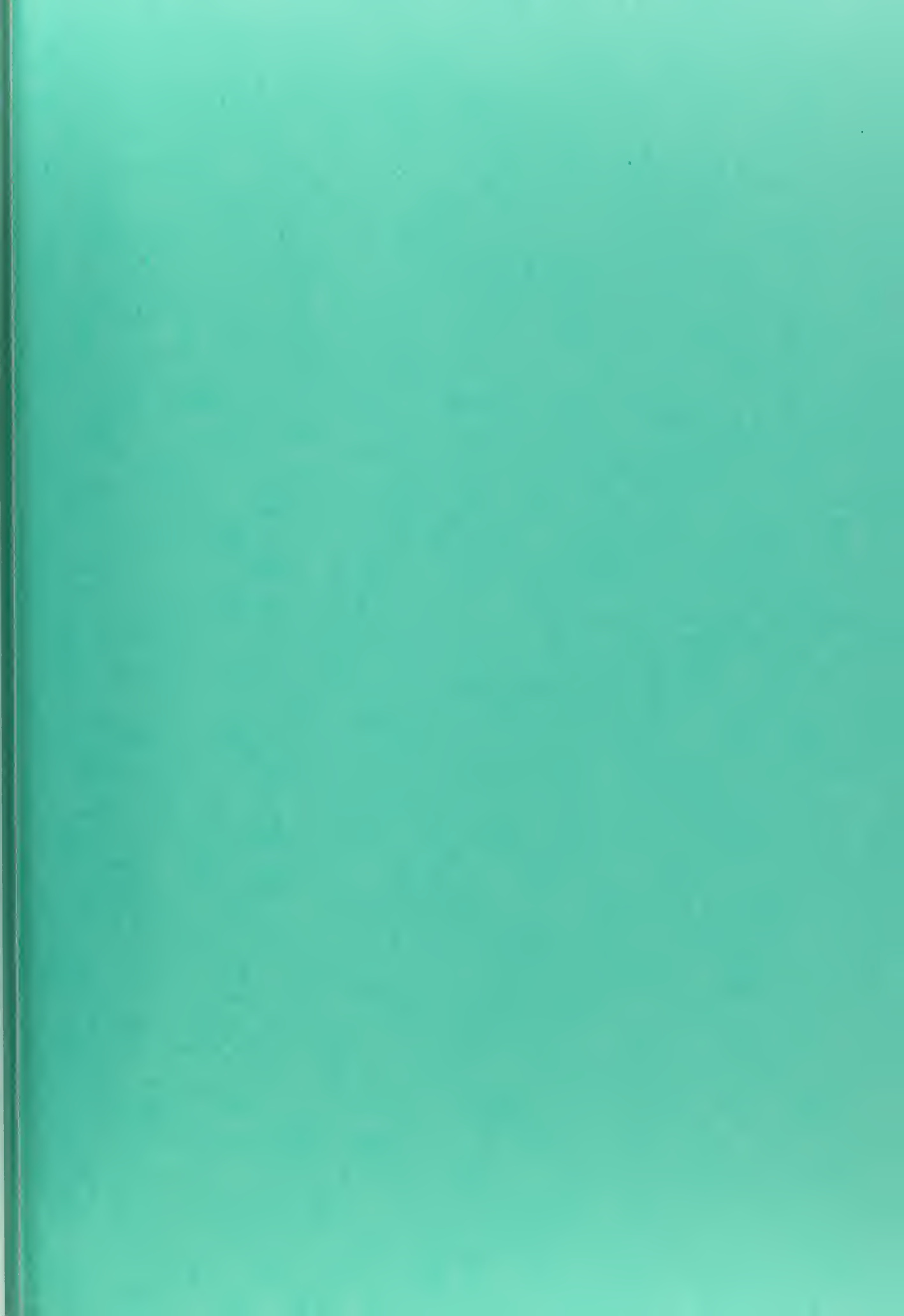
Figure 61. Histogram for zinc in stream sediments.

Table 11. Various parameters calculated on the basis of cumulative frequency curves.

Parameters	As (ppm)		Cd (ppm)		Cu (ppm)		Pb (ppm)		Hg (ppb)		p* (%)	Zn (ppm)	
	Stream Sediments	Bedrocks	Stream Sediments	Bedrocks	Stream Sediments	Bedrocks	Stream Sediments	Bedrocks	Stream Sediments	Bedrocks		Stream Sediments	Bedrocks
Arnold Level (t)	9.25	38.0	1.5	15.0	13.0	40.0	29.0	33.0	64.5	50.0	1.30	74.0	250.0
Geometric Mean (g)	1.4	7.0	0.2	5.2	5.1	19.0	7.9	20.0	23.4	12.5	0.52	21.5	40.0
Arithmetic Mean	2.4	10.8	1.4	27.2	7.6	30.7	9.7	21.0	21.3	27.2	2.66	26.6	46.0
Range	0-11.40	0-72	0-25.6	0-625	0-30	3-195	0-54	10-63	0-88	0.560	0.06-17.1	0-97	3-460
Normal Abundance (Lior, 1964)	1.8		0.2		55.0		12.5		80.0		0.105	70.0	
Abundance in Soils (Kogrador, 1959)	5.0		0.5		20.0		10.0		10.0		0.080	50.0	

based on analyses of only 97 samples.





**THIS BOOK IS DUE ON THE LAST DATE
STAMPED BELOW**

**BOOKS REQUESTED BY ANOTHER BORROWER
ARE SUBJECT TO RECALL AFTER ONE WEEK.
RENEWED BOOKS ARE SUBJECT TO
IMMEDIATE RECALL**

LIBRARY, UNIVERSITY OF CALIFORNIA, DAVIS

D4613 (12/76)



3 1175 00654 7163

